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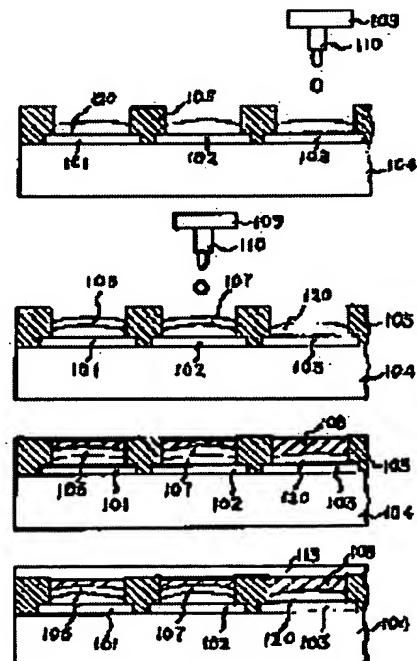
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(54) MANUFACTURE OF ORGANIC EL ELEMENT, ORGANIC EL ELEMENT, AND INK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide the manufacturing method of an organic EL (electroluminescent) element comprising an organic stacked film with low cost and high characteristics and provide an ink composition capable of manufacturing this organic EL element.

SOLUTION: This manufacturing method of an organic EL element having structure interposing a hole injection layer 120 and an luminescent layer 106 with an anode 101 and a cathode 113 has a process in which a hole injection layer 120 is formed by applying an ink composition containing a hole injection material made of an organic compound to a specified region on a substrate by an ink jet method; and a process in which luminescent layers 106, 107 are formed by applying an ink composition containing a luminescent material made of an organic compound by an ink jet method.



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JAPANESE

[JP,2000-323276,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the organic EL element characterized by to provide the process which applies the ink constituent containing the hole-injection material which is the manufacture method of the organic EL element of structure of having ****(ed) the hole-injection layer and the luminous layer by the anode plate and cathode, and becomes a predetermined field on a substrate from an organic compound with an ink-jet method, and forms a hole-injection layer, and the process which applies the ink constituent containing the luminescent material which consists of an organic compound with an ink-jet method, and forms a luminous layer.

[Claim 2] The manufacture method of the organic EL element according to claim 1 characterized by for the aforementioned organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this on a substrate, and forming the aforementioned hole-injection layer and the aforementioned luminous layer in the field between these septa.

[Claim 3] The manufacture method of the organic EL element according to claim 1 characterized by for the aforementioned organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this, and forming the aforementioned hole-injection layer and the aforementioned luminous layer through the consecutive-processing process of oxygen gas plasma and fluorocarbon gas plasma on a substrate.

[Claim 4] The manufacture method of the organic EL element according to claim 1 characterized by removing the solvent of this ink constituent after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound with an ink-jet method, removing the solvent of this ink constituent after applying the ink constituent containing obtaining a hole-injection layer and the luminescent material which consists of the aforementioned organic compound with an ink-jet method, and obtaining a luminous layer.

[Claim 5] Claim 1 written **** characterized by making the material of this ink constituent harden or conjugate with heat treatment further, and obtaining a luminous layer after applying the ink constituent characterized by providing the following with an ink-jet method ** which is made to harden or conjugate the material of this ink constituent with heat treatment further, and obtains a hole-injection layer after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound by the ink-jet method And luminescent-material ***** which consists of the aforementioned organic compound

[Claim 6] The manufacture method of an organic EL element given in either according to claim 1 to 5 which is characterized by the contact angle to the material from which the viscosity of the ink constituent containing the aforementioned hole-injection material or the aforementioned

luminescent material constitutes 1 – 20 mPa-s, and surface tension constitutes the nozzle side of 20 – 70 mN/m and an ink-jet head being 30–170 degrees.

[Claim 7] The manufacture method of the organic EL element according to claim 6 characterized by the solid part concentration of the aforementioned ink constituent being 0.01 – 10.0wt%.

[Claim 8] The organic EL element according to claim 6 or 7 characterized by the vapor pressure of the aforementioned ink constituent containing a kind of solvent of 0.001 – 50mmHg (room temperature) at least.

[Claim 9] The manufacture method of the organic EL element according to claim 8 characterized by the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[Claim 10] The manufacture method of the organic EL element according to claim 6 to 9 characterized by the aforementioned ink constituent containing a glycol-ether system acetic acid.

[Claim 11] the aforementioned ink constituent -- a lower alcohol -- less than [20wt%] -- the manufacture method of the organic EL element according to claim 6 to 10 characterized by containing

[Claim 12] The manufacture method of the organic EL element according to claim 6 characterized by the aforementioned ink constituent containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

[Claim 13] Furthermore, the manufacture method of the organic EL element according to claim 12 characterized by containing a silane coupling agent as a heat-curing agent.

[Claim 14] The manufacture method of the organic EL element according to claim 6 characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[Claim 15] The manufacture method of the organic EL element according to claim 14 characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

[Claim 16] The organic EL element manufactured by the method according to claim 1 to 15.

[Claim 17] The ink constituent characterized by being an ink constituent containing the hole-injection material or luminescent material applied by the ink-jet method in manufacture of an organic EL element, and the contact angle to the material from which viscosity constitutes 1 – 20 mPa-s, and surface tension constitutes the nozzle side of 20 – 70 mN/m and an ink-jet head being 30–170 degrees.

[Claim 18] The ink constituent according to claim 17 with which solid part concentration is characterized by ***** at 0.01 – 10.0wt%.

[Claim 19] The ink constituent according to claim 17 or 18 characterized by vapor pressure containing a kind of solvent of 0.001 – 50mmHg (room temperature) at least.

[Claim 20] They are the feature and an ink constituent according to claim 19 about the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[Claim 21] It is an ink constituent to the claim 17 characterized by including the aforementioned glycol-ether system acetic acid, or either of 20.

[Claim 22] a lower alcohol -- less than [20wt%] -- the ink constituent according to claim 17 to 21 characterized by containing

[Claim 23] The ink constituent according to claim 17 characterized by the aforementioned ink constituent containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

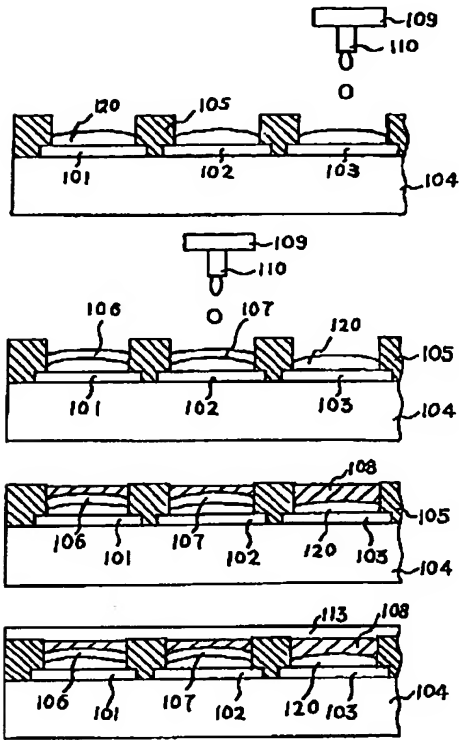
[Claim 24] Furthermore, the ink constituent according to claim 17 characterized by containing a silane coupling agent as a heat-curing agent.

[Claim 25] The ink constituent according to claim 17 characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[Claim 26] The ink constituent according to claim 25 characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

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Drawing selection [R pr sentativ drawing] ☐



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] It is related with the manufacture method of the organic EL element which is an electric light emitting device used for a display, the display light source, etc., an organic EL element, and the ink constituent used for the formation of a hole-injection layer or a luminous layer.

[0002]

[Description of the Prior Art] Development of the light emitting device which used the organic substance for the luminous layer as a spontaneous luminescence type display replaced with a liquid crystal display is accelerating in recent years. As a formation process of a luminous layer which consists of the organic substance in organic EL (electroluminescence) element, it is Appl.Phys.Lett.51(12) and 21. September How to form low-molecular material by the vacuum deposition as shown in 913 pages of 1987 Appl.Phys.Lett.71(1), 7 July The method of applying polymeric materials as shown from 34 pages of 1997 is mainly developed.

[0003] When using low-molecular system material as a means of colorization, the method of carrying out the vacuum evaporation of the luminescent material of the different luminescent color over the mask of a predetermined pattern to a desired pixel corresponding point, and forming it in it is performed. On the other hand, when using macromolecule system material, since patterning can be done minutely and easily, the colorization using the ink-jet method attracts attention. About production of the organic EL element by the ink-jet method, it is indicated by JP,7-235378,A, JP,10-12377,A, JP,10-153987,A, JP,11-40358,A, and JP,11-54270,A, for example.

[0004] Furthermore, by the organic EL element, in order to raise luminous efficiency and endurance, it is shown that a hole-injection layer or an electron hole transporting bed is formed between an anode plate and a luminous layer (Appl.Phys.Lett.51, 913 pages of 21 September 1987). Conventionally, a film is formed by the applying methods, such as a spin coat, using a conductive polymer, for example, the poly thiophene derivative, and the poly aniline derivative (357,477 Nature, 1992) as a buffer layer or a hole-injection layer. As the hole-injection layer or electron hole transporting bed of low-molecular system material, the phenylamine derivative was formed and used in many cases by vacuum evaporation.

[0005]

[Problem(s) to be Solved by the Invention] In the organic EL element, in case the laminated structure of a hole-injection layer and a luminous layer is formed, a means not to make material useless, but to carry out patterning of the organic thin film which constitutes a hole-injection layer and a luminous layer that it is simple and minutely, and to form membranes is demanded.

[0006] The ink-jet method is very effective. However, manufacture of the ink constituent which can form membranes as a functional film, without filling the stable regurgitation nature by the ink-jet method, and spoiling the property of material is a very difficult technical problem. The ink

constituent is indicated by JP,11-40358,A and JP,11-54270,A in manufacture of an organic EL element. The constituent which used high-boiling point solvents, such as a glycerol and a diethylene glycol, as DMF (dimethylformamide) or a wetting agent is indicated by these publications from the point of regurgitation nature. DMF has a problem in the stability over heat, an acid, and alkali, and higher alcohol, such as a glycerol and a diethylene glycol, has the problem which reacts in process of a PPV precursor and conjugation, and checks a property, when using a poly para-phenylene vinylene (PPV) as a green luminescent material. Moreover, especially a glycerol is difficult to remove.

[0007] Moreover, if the diameter of a nozzle tends to be made small and it is going to form a smaller ink-jet drop, in order to raise the resolution of patterning, the more a drop will become small, the more ink has also produced the problem of becoming easy to get dry.

[0008] Furthermore, when carrying out the laminating of the organic layer not only by the ink-jet method but by the applying method, the so-called compatibility in which the solvent of a constituent dissolves the organic film of a ground layer poses a problem. It is the case where a luminous layer is specifically formed on a hole-injection layer (or electron hole transporting bed).

[0009] Then, the place made into the technical problem of this invention is located in the place which provides the method row which manufactures the organic EL element which consists of an organic cascade screen which excelled [low cost / simplicity, a short time, and] in the property with the ink constituent which makes it possible.

[0010]

[Means for Solving the Problem] According to this invention, the manufacture method of the organic EL element of following the (1) - (5) is offered.

[0011] (1) The manufacture method of the organic EL element characterized by to provide the process which applies the ink constituent containing the hole-injection material which is the manufacture method of the organic EL element of structure of having ****(ed) the hole-injection layer and the luminous layer by the anode plate and cathode, and becomes a predetermined field on a substrate from an organic compound with an ink-jet method, and forms a hole-injection layer, and the process which applies the ink constituent containing the luminescent material which consists of an organic compound with an ink-jet method, and forms a luminous layer.

[0012] By the method of starting which forms both the hole-injection layer which consists of an organic compound, and a luminous layer by the ink-jet method, the method concerned can form all organic layers by the simple method, and can make any layer a high performance.

[0013] In addition, in this invention, a hole-injection layer is a layer into which an electron hole may be made to inject effective in a luminous layer from an anode plate side, and it also has an electron hole transportation function. Moreover, you may prepare the electron hole transporting bed which has an electron hole transportation function with a hole-injection layer in another layer.

[0014] (2) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this on a substrate, and forming the aforementioned hole-injection layer and the aforementioned luminous layer in the field between these septa.

[0015] A high definition organic EL element can be easily obtained with multiple color, without mixing a different luminous layer by the method concerned of (2).

[0016] (3) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this, and forming the aforementioned hole-injection layer and the aforementioned luminous layer through the consecutive-processing process of oxygen gas plasma and fluorocarbon gas plasma on a substrate.

[0017] By the method concerned of (3), the wettability difference in a drop can be given on a substrate, and detailed patterning of an ink-jet drop becomes possible.

[0018] (4) The manufacture method of the organic EL element of (1) characterized by removing the solvent of this ink constituent after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound with an ink-jet method, removing the solvent of this ink constituent after applying the ink constituent containing obtaining a hole-injection layer and the luminescent material which consists of the aforementioned organic compound with an ink-jet method, and obtaining a luminous layer.

[0019] The organic solid-state thin film as the desired hole-injection layer and desired luminous layer of a property can be formed by the method concerned of (4).

[0020] (5) The manufacture method of the organic EL element of (1) characterized by to make the material of this ink constituent harden or conjugate with heat treatment further, and to obtain a luminous layer after applying the ink constituent containing making the material of this ink constituent harden or conjugate with heat treatment further, and obtaining a hole-injection layer after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound by the ink-jet method, and the luminescent material which consists of the aforementioned organic compound with an ink-jet method.

[0021] The hole-injection layer and luminous layer which have the outstanding function by the method concerned of (5) can be formed.

[0022] Moreover, according to this invention, following (6) or the ink constituent of (15) is offered. (6) The ink constituent characterized by being an ink constituent containing the hole-injection material or luminescent material applied by the ink-jet method in manufacture of an organic EL element, and the contact angle to the material from which viscosity constitutes 1 – 20 mPa-s, and surface tension constitutes the nozzle side of 20 – 70 mN/m and an ink-jet head being 30–170 degrees.

[0023] the case where it applies especially by the ink-jet method according to the ink constituent concerned of (6) -- a nozzle -- while pressing down the blinding of a hole, and the flight deflection of an ink drop, the regurgitation is made smooth, and it becomes controllable [discharge quantity and regurgitation timing], and the stable regurgitation by the ink-jet method becomes possible

[0024] (7) (6) ink constituents with which solid part concentration is characterized by ***** at 0.01 – 10.0wt%.

[0025] According to the ink constituent concerned of (7), when applying by the ink-jet method, it becomes possible to obtain desired thickness, without spoiling regurgitation nature.

[0026] (8) (6) or (7) ink constituents which are characterized by vapor pressure containing a kind of solvent of 0.001 – 50mmHg (room temperature) at least.

[0027] the time of applying by the ink jet according to the ink constituent concerned of (8) -- dryness of ink -- it can stop -- a nozzle -- the blinding in a hole can be lost

(9) It is the ink constituent of the feature and either of (8) about the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[0028] In case the ink constituent concerned of (9) distributes or dissolves stably and is applied by the ink-jet method, without spoiling the property of hole-injection material or luminescent material, the stable regurgitation of it becomes possible.

[0029] (10) The ink constituent of either (6) characterized by including a glycol-ether system acetic acid, or (9).

[0030] It not only can suppress dryness of ink, but according to the ink constituent concerned of (10), it can improve membrane formation nature.

[0031] (11) a lower alcohol -- less than [20wt%] -- the ink constituent of either (6) characterized by containing, or (10)

[0032] According to the ink constituent concerned of (11), in case it applies especially by the ink-jet method, it becomes possible to adjust surface tension and viscosity to a desired value, without spoiling the regurgitation nature of ink.

[0033] (12) The ink constituent of (6) characterized by the aforementioned ink constituent

containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

[0034] According to the ink constituent concerned of (12), in case it applies especially by the ink-jet method, regurgitation nature and membrane formation nature are excellent, and it becomes possible to obtain a highly efficient hole-injection layer in an organic EL element.

[0035] (13) The ink constituent of (12) characterized by furthermore containing a silane coupling agent as a heat-curing agent.

[0036] If the ink constituent concerned of (13) is used, the hole-injection layer which does not cause compatibility with a luminous layer in an organic EL element by applying especially by the ink-jet method can be formed.

[0037] (14) The ink constituent of (6) characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[0038] According to the ink constituent concerned of (14), it can consider as the green which was excellent in the regurgitation nature at the time of applying especially to the ink-jet method, and membrane formation nature, and was excellent in the luminescence property in the organic EL element, or the ink constituent for red luminous layers.

[0039] (15) The ink constituent of (14) characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

[0040] According to the ink constituent concerned of (15), it can consider as the green which was excellent in the regurgitation nature at the time of applying especially to the ink-jet method, membrane formation nature, and the luminescence property, or the ink constituent for red luminous layers.

[0041] The above (6) or the ink constituent of (15) can be suitably used in the formation process of a hole-injection layer or a luminous layer in the manufacture method of the organic EL element of (1) or (5), respectively.

[0042] Moreover, according to this invention, the highly efficient organic EL element obtained by the above-mentioned method is offered.

[0043]

[Embodiments of the Invention] Hereafter, the operation gestalt of this invention is explained in detail.

[0044] It is the method of applying on the substrate which the ink constituent which made the solvent dissolve or distribute the hole-injection material which serves as the manufacture method of the organic EL element by the ink-jet method of this invention from the organic substance which forms an element, and the luminescent material which becomes a row from the organic substance is made to breathe out from an ink-jet head, for example, a transparent electrode is formed, and constitutes a pixel, and forming a luminous layer in a hole-injection layer row. According to this ink-jet method, detailed patterning can be performed simple in a short time, and multiple-color-izing is possible. Moreover, material is not made useless, even if it becomes the substrate of a large area, since what is necessary is just to apply the material of an initial complement to a required place.

[0045] The structure of the head for ink jets used for the organic EL element of this invention in the manufacture method is shown in drawing 1 and drawing 2 . The head 10 for ink jets concerned is equipped with the nozzle plate 11 and diaphragm 13 made from stainless steel, and both are joined through the batch member (reservoir plate) 15. between a nozzle plate 11 and diaphragms 13 -- a batch -- two or more ink rooms 19 and ***** 21 are formed of the member 15 The ink room 19 and the interior of ***** 21 are filled with the ink constituent of this invention, and the ink room 19 and ***** 21 are opening them for free passage through a feed hopper 23. furthermore, the nozzle for injecting an ink constituent from the ink room 19 in the shape of JIETO to a nozzle plate 11 -- the hole 25 is formed the ink introduction for on the other hand supplying an ink constituent to the head 10 for ink jets at ***** 21 -- the hole 27

is formed Moreover, on the field which counters the ink room 19 of a diaphragm 13, and the field of an opposite side, it is made to correspond to the position of the aforementioned space 19, and the piezoelectric device 29 is joined.

[0046] This piezoelectric device 29 is located between the electrodes 31 of a couple, and if it energizes, it will bend so that a piezoelectric device 29 may project outside. The capacity of the ink room 19 increases by this. Therefore, the ink constituent equivalent to a part for the capacity which increased in the ink room 19 flows through a feed hopper 23 from ***** 21.

Next, if the energization to a piezoelectric device 29 is canceled, both this piezoelectric device 29 and the diaphragm 13 will return to the original configuration. since space 19 also returns to the original capacity by this -- the pressure of the ink constituent of the ink room 19 interior -- going up -- a nozzle -- an ink constituent spouts towards a substrate from a hole 25

[0047] in addition, a nozzle -- the periphery of a hole 25 -- the flight deflection of an ink constituent, and a hole -- in order to prevent plugging, the ** ink layer 26 is formed namely, a nozzle -- the ** ink layer 26 which consists of a nickel-tetrafluoroethylene eutectoid deposit as the periphery of a hole 25 is shown in drawing 2 is formed

[0048] In the manufacture method of the organic EL element of this invention, the ink constituent containing the hole-injection material which is made to breathe out from the aforementioned head for ink jets, and is used, or luminescent material has the following properties.

[0049] The viscosity of an ink constituent is 1 – 20 mPa-s preferably, and is 2 – 8 mPa-s especially preferably. When the viscosity of an ink constituent is less than 1 mPa-s, solid part concentration becomes [too little] and control of discharge quantity not only becomes difficult, but may be unable to form enough films. the case where 20 mPa-s is exceeded -- a nozzle -- a possibility that an ink constituent cannot be made to breathe out smoothly from a hole -- it is -- a nozzle -- it may be necessary to change the specification of equipment, such as enlarging a hole case [furthermore,] viscosity is large -- a part for solid [in an ink constituent] -- depositing -- easy -- a nozzle -- the blinding frequency of a hole becomes high

[0050] Moreover, the surface tension of an ink constituent is 20 – 70 mN/m preferably, and is 25 – 45 mN/m especially preferably. By making it the surface tension of this range, the flight deflection in the case of the ink regurgitation can be stopped. the time of carrying out the regurgitation of the ink constituent, since the wettability on the nozzle side of an ink constituent will increase, if surface tension is less than 20 mN/m -- an ink constituent -- a nozzle -- it may adhere to the circumference of a hole asymmetrically in this case, a nozzle -- in order that attraction may work between the affixes made into the constituent adhering to the hole, and how to breathe out, the so-called flight deflection which will be breathed out by the uneven force and cannot reach a target position arises, and an ink constituent is natural -- the frequency also becomes high Moreover, since the configuration of the meniscus in the nose of cam of a nozzle will not be stabilized if 70 mN/m is exceeded, control of the discharge quantity of an ink constituent and regurgitation timing becomes difficult.

[0051] The contact angle to the material which constitutes the nozzle side which carries out the regurgitation of the ink constituent prepared in the head for ink jets is 30 degrees – 170 degrees preferably, and is 35 degrees – 65 degrees especially preferably. When an ink constituent has the contact angle of this range, the flight deflection of an ink constituent can be controlled and precise patterning becomes possible. Since the wettability to the material which constitutes the nozzle side of an ink constituent increases when this contact angle is less than 30 degrees, flight deflection arises like the case where it is surface tension. moreover . if it exceeds 170 degrees -- an ink constituent and a nozzle -- the interaction of a hole serves as the minimum, and since the configuration of the meniscus in the nose of cam of a nozzle is not stabilized, control of the discharge quantity of an ink constituent and regurgitation timing becomes difficult

[0052] Flight deflection means that the position which the dot reached produces a gap of 50

micrometers or more to a target position here, when an ink constituent is made to breathe out from the aforementioned nozzle. mainly -- a nozzle -- it generates by the case where the wettability of a hole is uneven, the blinding by adhesion of the solid component of an ink constituent, etc.

[0053] 0.01 – 10.0wt% of the solid part concentration of an ink constituent is desirable to the whole constituent, and is still more desirable. [0.1 – 5.0wt% of] If solid part concentration is too low, in order to obtain required thickness, the number of times of the regurgitation will increase and mass-production efficiency will become bad. Moreover, even if too high, viscosity becomes high and regurgitation nature is affected.

[0054] As for a part for the above-mentioned solid one, it is desirable for the vapor pressure in a room temperature to dissolve or distribute to at least one or more solvents of 0.005 – 50mmHg. using the solvent it is hard to become it dry -- an ink constituent -- a nozzle -- it can dry with a hole and can prevent adhesion for thickening, condensation, and solid taking place However, in membrane formation process, since removal of a solvent is difficult, a solvent with which vapor pressure is less than 0.005mmHg(s) is not suitable.

[0055] As such a solvent, glycol-ether system acetic acids, such as non-proton nature annular polar solvents, such as gamma-butyrolactone, N-methyl pyrrolidone (NMP), 1, and 3-dimethyl-2-imidazolidinone (DMI) and its derivative, or carbitol acetate (CA), and butyl carbitol acetate (BCA), are mentioned. Solvents, such as CA and BCA, are effective also at the point of raising membrane formation nature.

[0056] On the other hand, although lower alcohols, such as a methanol (MeOH), ethanol (EtOH), and propyl alcohol, are effective in manufacture of surface tension and viscosity, since volatility is high, it is desirable that it is less than [20wt%].

[0057] In addition, the above-mentioned property is suitable also as a property of the electron hole transportation material which constitutes this layer in the case of forming an electron hole transporting bed in an organic EL element.

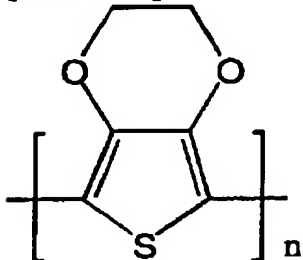
[0058] Hereafter, this invention is explained still in detail in accordance with an example.

[0059] (Example 1) An example 1 is related with the ink constituent for hole-injection stratification applied by the ink-jet method in manufacture of an organic EL element.

[0060] PEDT which is the poly thiophene derivative as a hole-injection material in this invention (polyethylene dioxythiophene)

[0061]

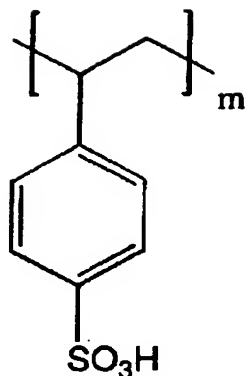
[Formula 1]



[0062] PSS (polystyrene sulfonic acid)

[0063]

[Formula 2]



[0064] ***** was used. These can be purchased from a Beyer company as BAITORONP. As a hole-injection material (or electron hole transportation material used as the material of an electron hole transporting bed), although the poly aniline, a porphyrin compound, a pyridine derivative, etc. are mentioned, it is the macromolecule which is thermally durable and BAITORON P which can be distributed to polar solvents, such as water, is suitable for the ink-jet method. The ink constituent shown in Table 1 using BAITORON P was prepared.

[0065]

[Table 1]

組成物	材料名	含有量 (wt%)
正孔注入／輸送材料	PEDT/PSS(バイトロンP)(水分散液)	7.25
極性溶媒	水	52.75
	メタノール	5
	イソプロピルアルコール	5
	1,3-ジメチル-2-イミダゾリジノン	30
シランカップリング剤	γ-グリシジルオキシプロピルトリメトキシシラン	0.08

[0066] In order to prevent compatibility with a luminous layer, the said weight addition was carried out with the conductive polymer, using gamma-glycidyloxypropyl trimethoxysilane as a silane coupling agent which constructs a bridge by heat-treatment. The solid part concentration of a final ink constituent was 0.16wt(s)%.

[0067] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink regurgitation nozzle side of the head for ink jets, regurgitation nature, patterning nature, and membrane formation nature is shown in Table 2. The following methods estimated the physical property and regurgitation property of an ink constituent.

[0068] Viscosity: The value in 20 degrees C was measured with E type viscometer.

[0069] Surface tension: Similarly the value in 20 degrees C was measured by the plate method.

[0070] Contact angle: It measured as a static contact angle on the material (nickel-tetrafluoroethylene eutectoid plating hydrophobic layer) which constitutes the ink regurgitation nozzle side of the head for ink jets.

[0071] Regurgitation property: The head for ink jet printers (Epson MJ-930C) was used. Flight deflection measured impact dispersion of the ink drop on the substrate when setting distance of a head and a substrate to 0.6mm. a nozzle -- a part for solid [of the ink constituent which carried out the continuation regurgitation (frequency of 7200Hz) of the ink constituent, and deposited as blinding frequency of a hole] etc. -- a nozzle -- the hole carried out blinding and the time taken to result in the state where it became regurgitation impotentia was measured

[0072] Patterning nature, membrane-formation nature: After breathing out to the test cell shown in drawing 3 (a) and (b) and removing a solvent in a room temperature and a vacuum, 200 degrees C (condensation, flat nature, etc.) of membraneous qualities of the film which heat-treated for 10 minutes and was formed were observed under the microscope among the atmosphere. A test cell has the pixel (40-micrometer pitch) which carried out opening of the

2-micrometer thick polyimide 40 formed on the ITO substrate 41 with the diameter of 30 micrometer. Performing consecutive processing of oxygen gas plasma and fluorocarbon gas plasma before the regurgitation, the polyimide front face used what hydrophilicity-ized ***** and the ITO front face. In addition, the aforementioned plasma treatment may be which atmosphere in a vacuum and the atmosphere. And the ink constituent 44 was breathed out from the ink-jet head 43 of ink-jet equipment 42 to opening, and the film was obtained and evaluated. A result is shown in the following table 2.

[0073]

[Table 2]

粘度 [mPa·s]	7.08
表面張力 [mN/m]	44.8
接触角 [°]	66
目詰まり頻度 [sec]	>10000
飛行ばらつき [μ m]	±20
パターニング性	○
成膜性	◎

[0074] As shown in Table 2, it was that to which regurgitation nature, patterning nature, and membrane formation nature reach sufficiency and practical use level. In addition, the place during composition of Table 1 (for example, the place which prepared the methanol (MeOH) and the constituent with which the addition of isopropyl alcohol (IPA) exceeds 20%, formed like the above, and was evaluated), or the place which prepared the constituent which did not add 1 and 3-dimethyl-2-imidazolidine (DMI), but was replaced with water, formed like the above, and was evaluated -- the above -- even if it fulfills a physical value, blinding has been started among the regurgitation by the thirst of an ink constituent

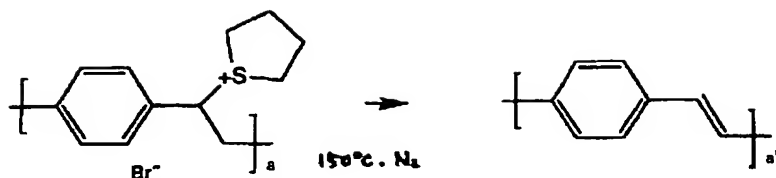
[0075] (Example 2) An example 2 is related with the ink constituent for luminous layers.

[0076] In this invention, poly (PARAFENIREMBINIREN) (PPV) was used as a green luminescent material.

[0077] as an organic compound which can form a luminous layer, the poly propine vinylenes, such as the poly alkyl thiophenes, such as PTV (poly (2, 5-thienylene vinylene)), PFV (poly (2, 5-FURIREN vinylene)), poly para-phenylene, and the poly alkyl fluorene, a pyrazoline dimer, a kino lysine carboxylic acid, benzo pyrylium perchlorate, a benzo PIRANO kino lysine, a phenanthroline europium complex, etc. mention other than PPV -- having -- these -- one sort -- or two or more sorts can be mixed and it What consists of a macromolecule organic compound also in these is desirable. A macromolecule organic compound is excellent in membrane formation nature, and the endurance of a luminous layer is very good. Macromolecule system material has molecular design tuck length latus flexibility, and the rational design of EL light emitting device is possible for it. Moreover, it has the band gap of a visible region, and comparatively high conductivity, and a conjugated-system macromolecule has such a remarkable inclination especially. As a luminous layer material, the precursor of the conjugated-system macromolecule which conjugates by the conjugated-system macromolecule itself or heating (membrane formation) is used. PPV or especially its derivative is desirable also in these. As a precursor of a PPV derivative, a MO-PPV (poly (2, 5-dimethoxy -1, 4-phenylenevinylene)) precursor, a CN-PPV (poly (2, 5-screw hexyloxy-1, 4-phenylene - (1-cyano vinylene))) precursor, etc. are mentioned. The precursor before conjugation (membrane formation) of PPV or its derivative is meltable to water or a polar solvent, and fits the pattern formation by the ink-jet method. Furthermore, PPV or its derivative has strong fluorescence, and since it is also the conductive polymer which the pi electron of a double bond has delocalized on a polymer chain, the thin film of PPV can function also as a hole-injection transporting bed, and can obtain a highly efficient organic EL element.

[0078]

[Formula 3]



[0079] The ink constituent shown in Table 3 using the poly (PARAFENIREMBINIREN) precursor (water / MeOH=5/95 mixed solution) was prepared. Solid part concentration was 0.3wt(s)%.

[0080]

[Table 3]

組成物	材料名	含有量 (wt%)
発光材料	PPV前駆体溶液 (1.5wt%)	20
	(水/メタノール=5/95 混合溶液)	
粘性増強	1,3-ジメチル-2-イミダゾリジノン	70
	ブチルカルビトールアセテート	10

[0081] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink regurgitation nozzle side of the head for ink jets, regurgitation nature, patterning nature, and membrane formation nature is shown in Table 4. The same method as an example 1 estimated the physical property and regurgitation property of an ink constituent. After the regurgitation, in the room temperature and the vacuum, membrane formation nature removed the solvent, among nitrogen-gas-atmosphere mind, 150 degrees C, is what was processed for 4 hours, and evaluated it.

[0082]

[Table 4]

粘度 [mPa·s]	3.21
表面張力 [mN/m]	37.6
接触角 [°]	58.6
目詰まり頻度 [sec]	>10000
飛行ばらつき [μm]	±25
パターンニング性	◎
成膜性	◎

[0083] As shown in Table 4, it was that to which regurgitation nature, patterning nature, and membrane formation nature reach sufficiency and practical use level. On the other hand, although it was satisfactory to regurgitation nature for example, when the ink constituent which replaced butyl carbitol acetate (BCA) with the glycerol was prepared and the same membrane formation and same evaluation as the above were performed or it replaced DMI by the dimethylformamide (DMF), luminous efficiency was low and also shifted the luminescent color to the short wavelength side. the case where he wants to make solid part concentration deeper than 0.3wt(s)% -- a precursor solution -- more than 20wt% -- if it adds -- a MeOH content -- increasing -- ink -- becoming it dry -- being easy -- since flight deflection and blinding were produced, what ****(ed) and condensed the precursor solution was used

[0084] (Example 3) An example 3 is related with the ink constituent for luminous layers.

[0085] In this example, what added the rhodamine 101 which is a low-molecular fluorochrome as a red luminescent material was used for the PPV precursor ink constituent used in the example 2.

[0086] The method of doping the fluorochrome of a low-molecular system can change the luminescence property of a luminous layer, for example, is very effective considering the improvement in luminous efficiency, or luminescence wavelength as a frog means. The high red of color purity and green luminescence can be obtained by the dope of a fluorochrome.

[0087] As a fluorochrome used for a red luminous layer, DCM of laser coloring matter, a rhodamine or a rhodamine derivative, a perylene, etc. can be used. Since it is low-molecular, it is

meltable to a solvent, and these fluorochromes have PPV etc. and good compatibility and formation of the uniform and stabilized luminous layer is easy for them. As a rhodamine derivative fluorochrome, Rhodamine B, the Rhodamine B base, rhodamine 6G, rhodamine 101 perchlorate, etc. are mentioned, for example, and two or more sorts of these may be mixed. [0088] Moreover, as a fluorochrome used for a green luminous layer, a Quinacridone, rubrene, DCJT(s), and those derivatives are mentioned. Like the above-mentioned red fluorochrome, since these fluorochromes are low-molecular, PPV etc. and compatibility are good meltable and formation of a luminous layer is easy for them to a solvent.

[0089] In this example, the ink constituent for red luminous layers shown in the following table 5 was prepared.

[0090]

[Table 5]

組成物	材料名	含有量 (wt%)
発光材料	PPV前駆体溶液 (1.5wt%) (水/メタノール=5/95 混合溶液)	20
	ローダミン101	0.0045 前駆体固型分比 1.5wt%
極性溶媒	1,3-ジメチル-2-イミダゾリジノン	70
	ブチルカルビトールアセテート	10

[0091] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink regurgitation nozzle side of the head for ink jets, regurgitation nature, patterning nature, and membrane formation nature is shown in Table 6. The same method as an example 2 estimated the physical property of an ink constituent and a regurgitation property, and membrane formation nature.

[0092]

[Table 6]

粘度 [mPa・s]	3.27
表面張力 [mN/m]	37.4
接触角 [°]	60
目詰まり順度 [sec]	>10000
飛行ばらつき [μm]	±25
パターンニング性	◎
成膜性	◎

[0093] As shown in Table 6, it was that to which regurgitation nature, patterning nature, and membrane formation nature reach sufficiency and practical use level. the amount of dopes of a rhodamine 101 -- a PPV precursor -- receiving -- 1.5wt(s)% -- when it added, it was the most efficient and red luminescence was shown

[0094] (Example 4) An example 4 is related with the manufacture method of the organic EL element by the ink-jet method. Drawing 4 shows the manufacturing process of the full color organic EL element of three colors.

[0095] While the transparent substrate 104 is a base material, it functions as a field which takes out light. Therefore, the transparent substrate 104 is chosen in consideration of the transparency property and thermal stability of light. As a transparent substrate material, although a glass substrate, transparent plastics, etc. are mentioned, for example, since it excels in thermal resistance, a glass substrate is desirable.

[0096] First, the pixel electrodes 101, 102, and 103 were formed on the transparent substrate 104. As the formation method, although photo lithography, vacuum deposition, the sputtering method, the metal-fog method, etc. are mentioned, for example, being based on photo lithography is desirable. As a pixel electrode, a transparent pixel electrode is desirable, and a tin-oxide film, an ITO film, the multiple-oxide film of indium oxide and a zinc oxide, etc. are mentioned as a material which constitutes a transparent pixel electrode.

[0097] Next, the septum (bank) 105 was formed by the photosensitive polyimide, and it buried each above transparent pixel inter-electrode. Thereby, improvement in contrast, prevention of the color mixture of luminescent material, the optical leak from between a pixel and pixels, etc. can be prevented.

[0098] although it obtains, and it will not be limited especially if it is, organic materials, such as acrylic resin, an epoxy resin, and a photosensitive polyimide, are desirable, for example from the thing which have endurance to the solvent of EL material as a material which constitutes a septum 105 and for which-izing can be carried out [Teflon] by fluorocarbon gas plasma treatment You may be the laminating septum which made inorganic material, such as liquefied glass, the lower layer. Moreover, a septum 105 mixes carbon black etc. in the above-mentioned material, and is good also as a black resist. As the formation method of this septum 105, photo lithography etc. is mentioned, for example.

[0099] Just before applying the ink constituent for hole-injection layers (further electron hole transporting bed), continuation plasma treatment of the oxygen gas of the above-mentioned substrate and fluorocarbon gas plasma was performed. Thereby, ***** and an ITO front face are hydrophilicity-ized and a polyimide front face can perform wettability control by the side of the substrate for carrying out patterning of the ink-jet drop minutely. As equipment which generates plasma, it can use similarly with the equipment which generates plasma in a vacuum, or the equipment which generates plasma in the atmosphere.

[0100] Next, the ink constituent for hole-injection layers mentioned in the example 1 was breathed out from the head 110 (Epson MJ-930C) of ink-jet print equipment 109, and the patterning application was performed on each pixel electrodes 101 and 102 and 103. The solvent was removed on a room temperature and the conditions of 20 minutes after an application and among the vacuum (1torr), and the ink constituent for luminous layers mentioned in the examples 2 and 3 and the hole-injection layer 120 not dissolving were formed among the atmosphere after that with 200 degrees C (on a hot plate), and heat treatment for 10 minutes. Thickness was 40nm. Although each pixel formed the common hole-injection layer in this example, depending on the case, you may form using the hole-injection material (or electron hole transportation material) which was suitable for the luminous layer the whole luminous layer.

[0101] The ink constituent for red luminous layers furthermore mentioned in the example 3 and the ink constituent for green luminous layers mentioned to the row in the example 2 were applied to the pixel electrode 101 row in the shape of PATANIN on 102 through the hole-injection layer 120 top with the ink-jet method. After an application and among the vacuum (1torr), the solvent was made to remove and conjugate continuously with 150 degrees C and heat treatment of 4 hours among nitrogen-gas-atmosphere mind on a room temperature and the conditions of 20 minutes, and the red luminous layer 106 and the green luminous layer 107 were formed. Thickness was 50nm. The luminous layer conjugated with heat treatment is insoluble to a solvent.

[0102] According to this ink-jet method, detailed patterning can be performed simple in a short time. Moreover, it is possible by changing the solid part concentration and discharge quantity of an ink constituent to change thickness.

[0103] Moreover, before forming a luminous layer, you may perform continuation plasma treatment of oxygen gas and fluorocarbon gas plasma in the hole-injection layer 120. A fluorine ghost layer is formed on a hole injection or the electron hole transporting bed 120 by this, and ionization potential can offer the incr ase of hole-injection efficiency, and the organic high EL element of luminous efficiency by the bird clapper highly.

[0104] Subsequently, the blue luminous layer 108 was formed on the pixel electrode 103 through the red luminous layer 106, green luminous layer 107, and hole-injection layer 120 top. Thereby, it not only forms the three primary colors of red, green, and blue, but it can bury and carry out flattening of the level difference of a red luminous layer and the 106 green luminous layer 107,

and a septum 105. Thereby, vertical inter-electrode short-circuit can be prevented certainly. By adjusting the thickness of a blue luminous layer, in a laminated structure with a red luminous layer and a green luminous layer, a blue luminous layer acts as an electron-injection transporting bed, and does not emit light blue.

[0105] It is not limited especially as the formation method of this blue luminous layer 108, but membranes can be formed also by the general spin coat method as a wet method, or the ink-jet method. In this example, the spin coat of the xylene solution of the poly dioctyl fluorene was carried out, and the blue luminous layer 108 of 45nm of thickness was formed.

[0106] The poly dihexyl fluorene which is otherwise the poly fluorene derivative as a blue luminous layer, and a copolymer with other polymerization machines are mentioned, and an organic compound with a blue fluorochrome or electron-injection transportation ability may be added.

[0107] As an organic compound which can form an electron-injection transporting bed, PBD, the OKISA diazole derivative of OXD-8 grade, DSA, an aluminum quinol complex, Bebq, a triazole derivative, an azomethine complex, a porphin complex, etc. are mentioned.

[0108] Since a full color organic EL element can be formed by combining with other organic luminescent material used for an ink-jet method even if it is the luminescent material which is seldom suitable for an ink-jet method by forming two colors with an ink-jet method among organic luminous layers, and forming other Isshiki by the conventional method of application like this example, the flexibility of an element design increases. As the conventional methods of application other than an ink-jet method, print processes, a replica method, a dipping method, the spin coat method, the cast method, the capillary-tube method, the roll coat method, the bar coat method, etc. are mentioned.

[0109] Finally, cathode (counterelectrode) 113 was formed. As cathode 113, a metal thin film electrode is desirable, and Mg, Ag, aluminum, Li, etc. are mentioned as a metal which constitutes cathode, for example. Moreover, the alloy which can use a small material of a work function other than these, for example, contains alkali metal, alkaline earth metal, such as calcium, and these can be used. Moreover, a metaled fluoridation object can also be adapted. Such cathode 113 can be formed by the vacuum deposition, the spatter, etc. In this example, calcium was carried out by the vacuum heating vacuum deposition, 1200nm laminating of the 100nm of the aluminum was further carried out by the spatter, and it considered as cathode.

[0110] Furthermore, you may form a protective coat on cathode 113. By forming a protective coat, cathode 113 and degradation of each luminous layers 106, 107, and 108, an injury, ablation, etc. were able to be prevented.

[0111] As a component of such a protective coat, an epoxy resin, acrylic resin, liquefied glass, etc. are mentioned. Moreover, as the formation method of a protective coat, the spin coat method, the casting method, a dipping method, the bar coat method, the roll coat method, the capillary-tube method, etc. are mentioned, for example.

[0112] In the organic EL element obtained by this example, two or more 100 cd/m brightness was obtained [the low battery not more than 5V] for the pixel of each color. Moreover, in the red pixel and green pixel which were formed with the ink-jet method, luminous efficiency was 0.15 lm/W and 0.25 lm/W, respectively, and the luminescence life (time when continuation luminescence is carried out, until it impresses fixed current, and it falls 50% to initial brightness) was also 2000 hours or more.

[0113] It was of the same grade as the thing of the red light emitting device which formed the hole-injection layer and the luminous layer by the same laminated structure on the spin coat using the same material as the above, and a green light emitting device. Thus, the property which was excellent also in the ink-jet method was able to be shown, and the element which is not inferior to a spin coat article was able to be formed.

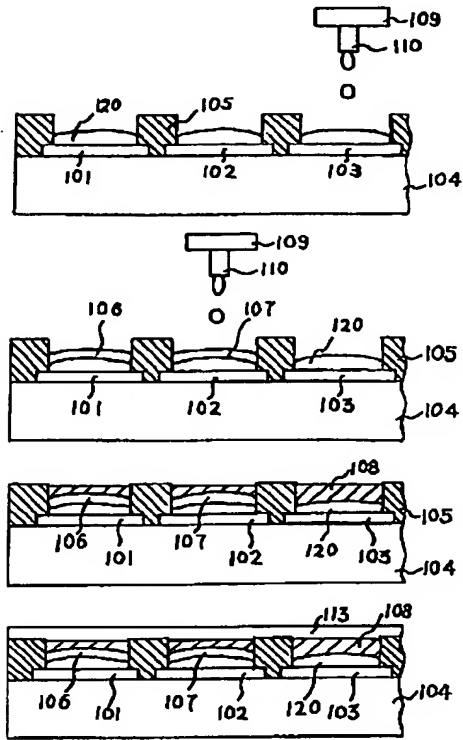
[0114]

[Effect of the Invention] Above, according to this invention, both a hole-injection layer and a

luminous layer can be formed by the ink-jet method, and an organic EL element can be obtained simply quickly by the low cost. Moreover, the ink constituent for hole injections and the ink constituent for luminescence material layers excellent in regurgitation nature, patterning nature, and membrane formation nature were able to be offered. Moreover, using this ink constituent, the pattern formation of a hole injection or an electron hole transporting bed, and the luminous layer can be carried out simple and easily with an ink-jet method, and the highly minute full color organic EL element which was excellent in the property which consists of a laminated structure can be manufactured.

[Translation done.]

Drawing selection [Repr sentativ drawing] ☐



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JAPANESE [JP,2000-323276,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
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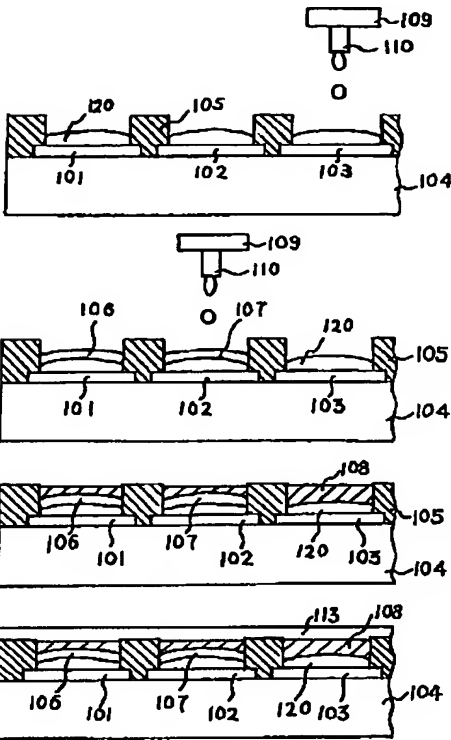
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TECHNICAL FIELD

[The technical field to which invention belongs] It is related with the manufacture method of the organic EL element which is an electric light emitting device used for a display, the display light source, etc., an organic EL element, and the ink constituent used for the formation of a hole-injection layer or a luminous layer.

[Translation done.]

Drawing selection [Representative drawing] 



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PRIOR ART

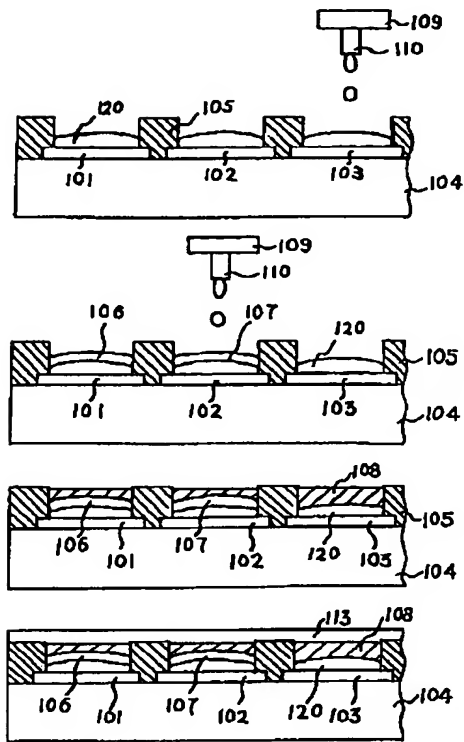
[Description of the Prior Art] Development of the light emitting device which used the organic substance for the luminous layer as a spontaneous luminescence type display replaced with a liquid crystal display is accelerating in recent years. As a formation process of a luminous layer which consists of the organic substance in organic EL (electroluminescence) element, it is Appl.Phys.Lett.51(12) and 21. September How to form low-molecular material by the vacuum deposition as shown in 913 pages of 1987 Appl.Phys.Lett.71(1), 7 July The method of applying polymeric materials as shown from 34 pages of 1997 is mainly developed.

[0003] When using low-molecular system material as a means of colorization, the method of carrying out the vacuum evaporation of the luminescent material of the different luminescent color over the mask of a predetermined pattern to a desired pixel corresponding point, and forming it in it is performed. On the other hand, when using macromolecule system material, since patterning can be done minutely and easily, the colorization using the ink-jet method attracts attention. About production of the organic EL element by the ink-jet method, it is indicated by JP,7-235378,A, JP,10-12377,A, JP,10-153987,A, JP,11-40358,A, and JP,11-54270,A, for example.

[0004] Furthermore, by the organic EL element, in order to raise luminous efficiency and endurance, it is shown that a hole-injection layer or an electron hole transporting bed is formed between an anode plate and a luminous layer (Appl.Phys.Lett.51, 913 pages of 21 September 1987). Conventionally, a film is formed by the applying methods, such as a spin coat, using a conductive polymer, for example, the poly thiophene derivative, and the poly aniline derivative (357,477 Nature, 1992) as a buffer layer or a hole-injection layer. As the hole-injection layer or electron hole transporting bed of low-molecular system material, the phenylamine derivative was formed and used in many cases by vacuum evaporation.

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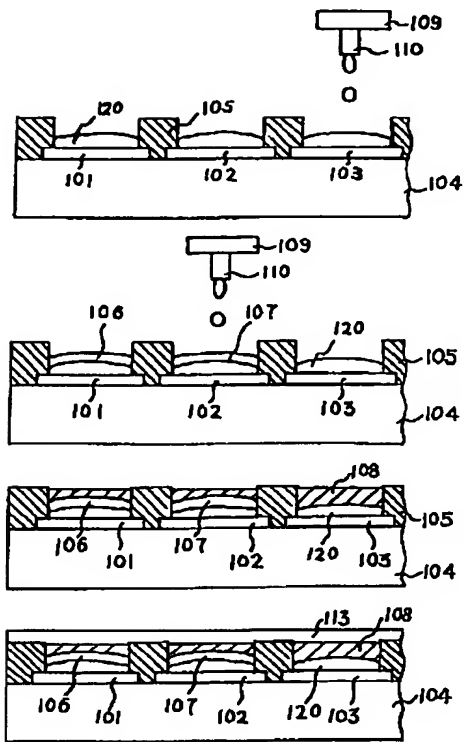
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EFFECT OF THE INVENTION

[Effect of the Invention] Above, according to this invention, both a hole-injection layer and a luminous layer can be formed by the ink-jet method, and an organic EL element can be obtained simply quickly by the low cost. Moreover, the ink constituent for hole injections and the ink constituent for luminescence material layers excellent in *****, patterning nature, and membrane formation nature were able to be offered. Moreover, using this ink constituent, the pattern formation of a hole injection or an electron hole transporting bed, and the luminous layer can be carried out simple and easily with an ink-jet method, and the highly minute full color organic EL element which was excellent in the property which consists of a laminated structure can be manufactured.

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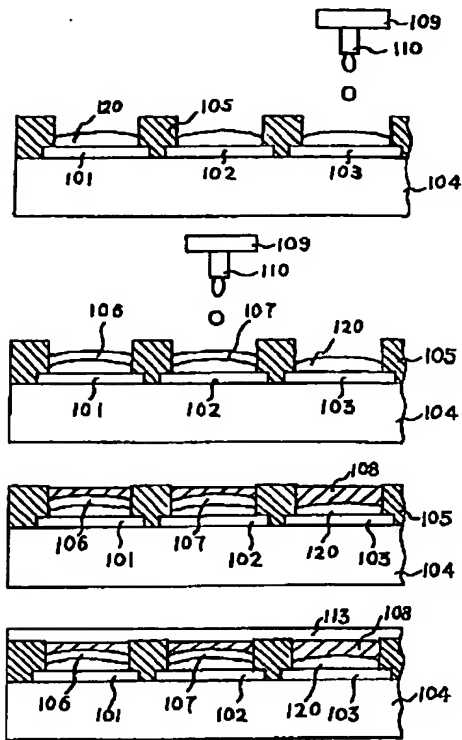
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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In the organic EL element, in case the laminated structure of a hole-injection layer and a luminous layer is formed, a means not to make material useless, but to carry out patterning of the organic thin film which constitutes a hole-injection layer and a luminous layer that it is simple and minutely, and to form membranes is demanded. [0006] The ink-jet method is very effective. However, manufacture of the ink constituent which can form membranes as a functional film, without filling the stable regurgitation nature by the ink-jet method, and spoiling the property of material is a very difficult technical problem. The ink constituent is indicated by JP,11-40358,A and JP,11-54270,A in manufacture of an organic EL element. The constituent which used high-boiling point solvents, such as a glycerol and a diethylene glycol, as DMF (dimethylformamide) or a wetting agent is indicated by these publications from the point of regurgitation nature. DMF has a problem in the stability over heat, an acid, and alkali, and higher alcohol, such as a glycerol and a diethylene glycol, has the problem which reacts in process of a PPV precursor and conjugation, and checks a property, when using a poly para-phenylene vinylene (PPV) as a green luminescent material. Moreover, especially a glycerol is difficult to remove. [0007] Moreover, if the diameter of a nozzle tends to be made small and it is going to form a smaller ink-jet drop, in order to raise the resolution of patterning, the more a drop will become small, the more ink has also produced the problem of becoming easy to get dry. [0008] Furthermore, when carrying out the laminating of the organic layer not only by the ink-jet method but by the applying method, the so-called compatibility in which the solvent of a constituent dissolves the organic film of a ground layer poses a problem. It is the case where a luminous layer is specifically formed on a hole-injection layer (or electron hole transporting bed). [0009] Then, the place made into the technical problem of this invention is located in the place which provides the method row which manufactures the organic EL element which consists of an organic cascade screen which excelled [low cost / simplicity, a short time, and] in the property with the ink constituent which makes it possible.

[Translation done.]

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MEANS

[Means for Solving the Problem] According to this invention, the manufacture method of the organic EL element of following the (1) – (5) is offered.

[0011] (1) The manufacture method of the organic EL element characterized by to provide the process which applies the ink constituent containing the hole-injection material which is the manufacture method of the organic EL element of structure of having ****(ed) the hole-injection layer and the luminous layer by the anode plate and cathode, and becomes a predetermined field on a substrate from an organic compound with an ink-jet method, and forms a hole-injection layer, and the process which applies the ink constituent containing the luminescent material which consists of an organic compound with an ink-jet method, and forms a luminous layer.

[0012] By the method of starting which forms both the hole-injection layer which consists of an organic compound, and a luminous layer by the ink-jet method, the method concerned can form all organic layers by the simple method, and can make any layer a high performance.

[0013] In addition, in this invention, a hole-injection layer is a layer into which an electron hole may be made to inject effective in a luminous layer from an anode plate side, and it also has an electron hole transportation function. Moreover, you may prepare the electron hole transporting bed which has an electron hole transportation function with a hole-injection layer in another layer.

[0014] (2) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this on a substrate, and forming the aforementioned hole-injection layer and the aforementioned luminous layer in the field between these septa.

[0015] A high definition organic EL element can be easily obtained with multiple color, without mixing a different luminous layer by the method concerned of (2).

[0016] (3) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this, and forming the aforementioned hole-injection layer and the aforementioned luminous layer through the consecutive-processing process of oxygen gas plasma and fluorocarbon gas plasma on a substrate.

[0017] By the method concerned of (3), the wettability difference in a drop can be given on a substrate, and detailed patterning of an ink-jet drop becomes possible.

[0018] (4) The manufacture method of the organic EL element of (1) characterized by removing the solvent of this ink constituent after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound with an ink-jet method, removing the solvent of this ink constituent after applying the ink constituent containing obtaining a hole-injection layer and the luminescent material which consists of the aforementioned organic compound with an ink-jet method, and obtaining a luminous layer.

[0019] The organic solid-state thin film as the desired hole-injection layer and desired luminous

layer of a property can be formed by the method concerned of (4).

[0020] (5) The manufacture method of the organic EL element of (1) characterized by to make the material of this ink constituent harden or conjugate with heat treatment further, and to obtain a luminous layer after applying the ink constituent containing making the material of this ink constituent harden or conjugate with heat treatment further, and obtaining a hole-injection layer after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound by the ink-jet method, and the luminescent material which consists of the aforementioned organic compound with an ink-jet method.

[0021] The hole-injection layer and luminous layer which have the outstanding function by the method concerned of (5) can be formed.

[0022] Moreover, according to this invention, following (6) or the ink constituent of (15) is offered. (6) The ink constituent characterized by being an ink constituent containing the hole-injection material or luminescent material applied by the ink-jet method in manufacture of an organic EL element, and the contact angle to the material from which viscosity constitutes 1 – 20 mPa·s, and surface tension constitutes the nozzle side of 20 – 70 mN/m and an ink-jet head being 30–170 degrees.

[0023] the case where it applies especially by the ink-jet method according to the ink constituent concerned of (6) -- a nozzle -- while pressing down the blinding of a hole, and the flight deflection of an ink drop, the regurgitation is made smooth, and it becomes controllable [discharge quantity and regurgitation timing], and the stable regurgitation by the ink-jet method becomes possible

[0024] (7) (6) ink constituents with which solid part concentration is characterized by ***** at 0.01 – 10.0wt%.

[0025] According to the ink constituent concerned of (7), when applying by the ink-jet method, it becomes possible to obtain desired thickness, without spoiling regurgitation nature.

[0026] (8) (6) or (7) ink constituents which are characterized by vapor pressure containing a kind of solvent of 0.001 – 50mmHg (room temperature) at least.

[0027] the time of applying by the ink jet according to the ink constituent concerned of (8) -- dryness of ink -- it can stop -- a nozzle -- the blinding in a hole can be lost

(9) It is the ink constituent of the feature and either of (8) about the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[0028] In case the ink constituent concerned of (9) distributes or dissolves stably and is applied by the ink-jet method, without spoiling the property of hole-injection material or luminescent material, the stable regurgitation of it becomes possible.

[0029] (10) The ink constituent of either (6) characterized by including a glycol-ether system acetic acid, or (9).

[0030] It not only can suppress dryness of ink, but according to the ink constituent concerned of (10), it can improve membrane formation nature.

[0031] (11) a lower alcohol -- less than [20wt%] -- the ink constituent of either (6) characterized by containing, or (10)

[0032] According to the ink constituent concerned of (11), in case it applies especially by the ink-jet method, it becomes possible to adjust surface tension and viscosity to a desired value, without spoiling the regurgitation nature of ink.

[0033] (12) The ink constituent of (6) characterized by the aforementioned ink constituent containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

[0034] According to the ink constituent concerned of (12), in case it applies especially by the ink-jet method, ***** and membrane formation nature are excellent and it becomes possible to obtain a highly efficient hole-injection layer in an organic EL element.

[0035] (13) The ink constituent of (12) characterized by furthermore containing a silane coupling agent as a heat-curing agent.

[0036] If the ink constituent concerned of (13) is used, the hole-injection layer which does not cause compatibility with a luminous layer in an organic EL element by applying especially by the ink-jet method can be formed.

[0037] (14) The ink constituent of (6) characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[0038] According to the ink constituent concerned of (14), it can consider as the green which was excellent in ***** at the time of applying especially to the ink-jet method, and membrane formation nature, and was excellent in the luminescence property in the organic EL element, or the ink constituent for red luminous layers.

[0039] (15) The ink constituent of (14) characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

[0040] According to the ink constituent concerned of (15), it can consider as the green which was excellent in ***** at the time of applying especially to the ink-jet method, membrane formation nature, and the luminescence property, or the ink constituent for red luminous layers.

[0041] The above (6) or the ink constituent of (15) can be suitably used in the formation process of a hole-injection layer or a luminous layer in the manufacture method of the organic EL element of (1) or (5), respectively.

[0042] Moreover, according to this invention, the highly efficient organic EL element obtained by the above-mentioned method is offered.

[0043]

[Embodiments of the Invention] Hereafter, the operation form of this invention is explained in detail.

[0044] It is the method of applying on the substrate which the ink constituent which made the solvent dissolve or distribute the hole-injection material which serves as the manufacture method of the organic EL element by the ink-jet method of this invention from the organic substance which forms an element, and the luminescent material which becomes a row from the organic substance is made to breathe out from an ink-jet head, for example, a transparent electrode is formed, and constitutes a pixel, and forming a luminous layer in a hole-injection layer row. According to this ink-jet method, detailed patterning can be performed simple in a short time, and multiple-color-izing is possible. Moreover, material is not made useless, even if it becomes the substrate of a large area, since what is necessary is just to apply the material of an initial complement to a required place.

[0045] The structure of the head for ink jets used for the organic EL element of this invention in the manufacture method is shown in drawing 1 and drawing 2 . The head 10 for ink jets concerned is equipped with the nozzle plate 11 and diaphragm 13 made from stainless steel, and both are joined through the batch member (reservoir plate) 15. between a nozzle plate 11 and diaphragms 13 -- a batch -- two or more ink rooms 19 and ***** 21 are formed of the member 15 The ink room 19 and the interior of ***** 21 are filled with the ink constituent of this invention, and the ink room 19 and ***** 21 are opening them for free passage through a feed hopper 23. furthermore, the nozzle for injecting an ink constituent from the ink room 19 in the shape of JIETO to a nozzle plate 11 -- the hole 25 is formed the ink introduction for on the other hand supplying an ink constituent to the head 10 for ink jets at ***** 21 -- the hole 27 is formed Moreover, on the field which counters the ink room 19 of a diaphragm 13, and the field of an opposite side, it is made to correspond to the position of the aforementioned space 19, and the piezoelectric device 29 is joined.

[0046] This piezoelectric device 29 is located between the electrodes 31 of a couple, and if it energizes, it will bend so that a piezoelectric device 29 may project outside. The capacity of the ink room 19 increases by this. Therefore, the ink constituent equivalent to a part for the capacity which increased in the ink room 19 flows through a feed hopper 23 from ***** 21. Next, if the energization to a piezoelectric device 29 is canceled, both this piezoelectric device

29 and the diaphragm 13 will return to the original configuration. since space 19 also returns to the original capacity by this -- the pressure of the ink constituent of the ink room 19 interior -- going up -- a nozzle -- an ink constituent spouts towards a substrate from a hole 25

[0047] in addition, a nozzle -- the periphery of a hole 25 -- the flight deflection of an ink constituent, and a hole -- in order to prevent plugging, the ** ink layer 26 is formed namely, a nozzle -- the ** ink layer 26 which consists of a nickel-tetrafluoroethylene eutectoid deposit as the periphery of a hole 25 is shown in drawing 2 is formed

[0048] In the manufacture method of the organic EL element of this invention, the ink constituent containing the hole-injection material which is made to breathe out from the aforementioned head for ink jets, and is used, or luminescent material has the following properties.

[0049] The viscosity of an ink constituent is 1 – 20 mPa-s preferably, and is 2 – 8 mPa-s especially preferably. When the viscosity of an ink constituent is less than 1 mPa-s, solid part concentration becomes [too little] and control of discharge quantity not only becomes difficult, but may be unable to form enough films. the case where 20 mPa-s is exceeded -- a nozzle -- a possibility that an ink constituent cannot be made to breathe out smoothly from a hole -- it is -- a nozzle -- it may be necessary to change the specification of equipment, such as enlarging a hole case [furthermore,] viscosity is large -- a part for solid [in an ink constituent] -- depositing -- easy -- a nozzle -- the blinding frequency of a hole becomes high

[0050] Moreover, the surface tension of an ink constituent is 20 – 70 mN/m preferably, and is 25 – 45 mN/m especially preferably. By making it the surface tension of this range, the flight deflection in the case of ink **** can be stopped. the ** time which breathes out an ink constituent since the wettability on the nozzle side of an ink constituent will increase, if surface tension is less than 20 mN/m -- an ink constituent -- a nozzle -- it may adhere to the circumference of a hole asymmetrically in this case, a nozzle -- in order that attraction may work between the affixes made into the constituent adhering to the hole, and how to breathe out, the so-called flight deflection which will be breathed out by the uneven force and cannot reach a target position arises, and an ink constituent is natural -- the frequency also becomes high Moreover, since the configuration of the meniscus in the nose of cam of a nozzle will not be stabilized if 70 mN/m is exceeded, control of the discharge quantity of an ink constituent and **** timing becomes difficult.

[0051] The contact angle to the material which constitutes the ** nozzle side which breathes out the ink constituent prepared in the head for ink jets is 30 degrees – 170 degrees preferably, and is 35 degrees – 65 degrees especially preferably. When an ink constituent has the contact angle of this range, the flight deflection of an ink constituent can be controlled and precise patterning becomes possible. Since the wettability to the material which constitutes the nozzle side of an ink constituent increases when this contact angle is less than 30 degrees, flight deflection arises like the case where it is surface tension. moreover . if it exceeds 170 degrees -- an ink constituent and a nozzle -- the interaction of a hole serves as the minimum, and since the configuration of the meniscus in the nose of cam of a nozzle is not stabilized, control of the discharge quantity of an ink constituent and **** timing becomes difficult

[0052] Flight deflection means that the position which the dot reached produces a gap of 50 micrometers or more to a target position here, when an ink constituent is made to breathe out from the aforementioned nozzle. mainly -- a nozzle -- it generates by the case where the wettability of a hole is uneven, the blinding by adhesion of the solid component of an ink constituent, etc.

[0053] 0.01 – 10.0wt% of the solid part concentration of an ink constituent is desirable to the whole constituent, and is still more desirable. [0.1 – 5.0wt% of] If solid part concentration is too low, in order to obtain required thickness, the number of times of **** will increase and mass-production efficiency will become bad. Moreover, even if too high, viscosity becomes high and ***** is affected.

[0054] As for a part for the above-mentioned solid one, it is desirable for the vapor pressure in a room temperature to dissolve or distribute to at least one or more solvents of 0.005 – 50mmHg. using the solvent it is hard to become it dry -- an ink constituent -- a nozzle -- it can dry with a hole and can prevent adhesion for thickening, condensation, and solid taking place However, in membrane formation process, since removal of a solvent is difficult, a solvent with which vapor pressure is less than 0.005mmHg(s) is not suitable.

[0055] As such a solvent, glycol-ether system acetic acids, such as non-proton nature annular polar solvents, such as gamma-butyrolactone, N-methyl pyrrolidone (NMP), 1, and 3-dimethyl-2-imidazolidinone (DMI) and its derivative, or carbitol acetate (CA), and butyl carbitol acetate (BCA), are mentioned. Solvents, such as CA and BCA, are effective also at the point of raising membrane formation nature.

[0056] On the other hand, although lower alcohols, such as a methanol (MeOH), ethanol (EtOH), and propyl alcohol, are effective in manufacture of surface tension and viscosity, since volatility is high, it is desirable that it is less than [20wt%].

[0057] In addition, the above-mentioned property is suitable also as a property of the electron hole transportation material which constitutes this layer in the case of forming an electron hole transporting bed in an organic EL element.

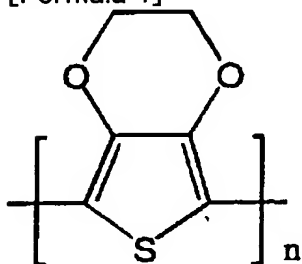
[0058] Hereafter, this invention is explained still in detail in accordance with an example.

[0059] (Example 1) An example 1 is related with the ink constituent for hole-injection layer formation applied by the ink-jet method in manufacture of an organic EL element.

[0060] PEDT which is the poly thiophene derivative as a hole-injection material in this invention (polyethylene dioxythiophene)

[0061]

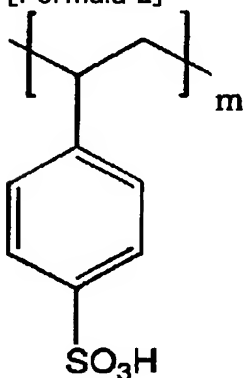
[Formula 1]



[0062] PSS (polystyrene sulfonic acid)

[0063]

[Formula 2]



[0064] ***** was used. These can be purchased from a Beyer company as BAITORONP. As a hole-injection material (or electron hole transportation material used as the material of an electron hole transporting bed), although the poly aniline, a porphyrin compound, a pyridine derivative, etc. are mentioned, it is the macromolecule which is thermally durable and BAITORON P which can be distributed to polar solvents, such as water, is suitable for the

ink-jet method. The ink constituent shown in Table 1 using BAITORON P was prepared.

[0065]

[Table 1]

組成物	材料名	含有量 (wt%)
正孔注入／輸送材料	PEDT/PSS(バイトロンP)(水分散液)	7.25
極性溶媒	水	52.75
	メタノール	5
	イソプロピルアルコール	5
	1,3-ジメチル-2-イミダゾリジノン	30
シランカップリング剤	γ-グリシジルオキシプロピルトリメトキシシラン	0.08

[0066] In order to prevent compatibility with a luminous layer, the said weight addition was carried out with the conductive polymer, using gamma-glycidyloxypropyl trimethoxysilane as a silane coupling agent which constructs a bridge by heat-treatment. The solid part concentration of a final ink constituent was 0.16wt(s)%.

[0067] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink **** nozzle side of the head for ink jets, *****, patterning nature, and membrane formation nature is shown in Table 2. The following methods estimated the physical property and **** property of an ink constituent.

[0068] Viscosity: The value in 20 degrees C was measured with E type viscometer.

[0069] Surface tension: Similarly the value in 20 degrees C was measured by the plate method.

[0070] Contact angle: It measured as a static contact angle on the material (nickel-tetrafluoroethylene eutectoid plating hydrophobic layer) which constitutes the ink **** nozzle side of the head for ink jets.

[0071] **** property: The head for ink jet printers (Epson MJ-930C) was used. Flight deflection measured impact dispersion of the ink drop on the substrate when setting distance of a head and a substrate to 0.6mm. a nozzle -- a part for solid [of the ink constituent which carried out continuation **** (frequency of 7200Hz) of the ink constituent, and deposited as blinding frequency of a hole] etc. -- a nozzle -- the hole carried out blinding and the time taken to result in the state where **** became impossible was measured

[0072] Patterning nature, membrane-formation nature: After breathing out to the test cell shown in drawing 3 (a) and (b) and removing a solvent in a room temperature and a vacuum, 200 degrees C (condensation, flat nature, etc.) of membraneous qualities of the film which heat-treated for 10 minutes and was formed were observed under the microscope among the atmosphere. A test cell has the pixel (40-micrometer pitch) which carried out opening of the 2-micrometer thick polyimide 40 formed on the ITO substrate 41 with the diameter of 30 micrometer. Performing consecutive processing of oxygen gas plasma and fluorocarbon gas plasma to *****, the polyimide front face used what hydrophilicity-ized ***** and the ITO front face. In addition, the aforementioned plasma treatment may be which atmosphere in a vacuum and the atmosphere. And the ink constituent 44 was breathed out from the ink-jet head 43 of ink-jet equipment 42 to opening, and the film was obtained and evaluated. A result is shown in the following table 2.

[0073]

[Table 2]

粘度 [mPa・s]	7.08
表面張力 [mN/m]	44.9
接触角 [°]	65
目詰まり頻度 [sec]	>10000
飛行ばらつき [μm]	±20
パターンニング性	
成膜性	

[0074] As shown in Table 2, it was that to which *****, patterning nature, and membrane formation nature reach sufficiency and practical use level. In addition, the place during

composition of Table 1 (for example, the place which prepared the methanol (MeOH) and the constituent with which the addition of isopropyl alcohol (IPA) exceeds 20%, formed like the above, and was evaluated), or the place which prepared the constituent which did not add 1 and 3-dimethyl-2-imidazolidine (DMI), but was replaced with water, formed like the above, and was evaluated -- the above -- even if it fulfills a physical value, blinding has been started among **** by thirst of an ink constituent

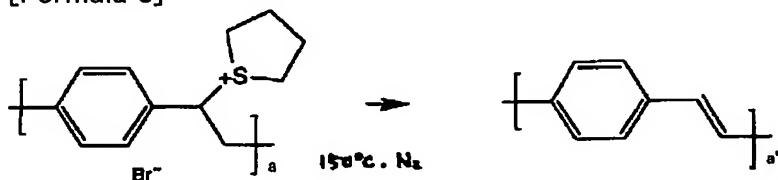
[0075] (Example 2) An example 2 is related with the ink constituent for luminous layers.

[0076] In this invention, poly (PARAFENIREMBINIREN) (PPV) was used as a green luminescent material.

[0077] as an organic compound which can form a luminous layer, the poly propine vinylenes, such as the poly alkyl thiophenes, such as PTV (poly (2, 5-thienylene vinylene)), PFV (poly (2, 5-FURIREN vinylene)), poly para-phenylene, and the poly alkyl fluorene, a pyrazoline dimer, a KINORI gin carboxylic acid, benzo pyrylium perchlorate, a benzo peeler NOKINO lysine, a phenanthroline europium complex, etc. mention other than PPV -- having -- these -- one sort -- or two or more sorts can be mixed and it What consists of a macromolecule organic compound also in these is desirable. A macromolecule organic compound is excellent in membrane formation nature, and the endurance of a luminous layer is very good. Macromolecule system material has broad flexibility on a molecular design, and the rational design of EL light emitting device is possible for it. Moreover, it has the band gap of a visible region, and comparatively high conductivity, and a conjugated-system macromolecule has such a remarkable inclination especially. As a luminous layer material, the precursor of the conjugated-system macromolecule which conjugates by the conjugated-system macromolecule itself or heating (membrane formation) is used. PPV or especially its derivative is desirable also in these. As a precursor of a PPV derivative, a MO-PPV (poly (2, 5-dimethoxy -1, 4-phenylenevinylene)) precursor, a CN-PPV (poly (2, 5-screw hexyloxy-1, 4-phenylene - (1-cyano vinylene))) precursor, etc. are mentioned. The precursor before conjugation (membrane formation) of PPV or its derivative is meltable to water or a polar solvent, and fits the pattern formation by the ink-jet method. Furthermore, PPV or its derivative has strong fluorescence, and since it is also the conductive polymer which the pi electron of a double bond has delocalized on a polymer chain, the thin film of PPV can function also as a hole-injection transporting bed, and can obtain a highly efficient organic EL element.

[0078]

[Formula 3]



[0079] The ink constituent shown in Table 3 using the poly (PARAFENIREMBINIREN) precursor (water / MeOH=5/95 mixed solution) was prepared. Solid part concentration was 0.3wt(s)%.

[0080]

[Table 3]

組成物	材料名	含有量 (wt%)
発光材料	PPV前駆体溶液 (1.5wt%)	20
	(水/メタノール=5/95 混合溶液)	
粘性増強	1,3-ジメチル-2-イミダゾリジノン	70
	ブチルカルビトールアセテート	10

[0081] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink **** nozzle side of the head for ink jets, *****, patterning nature, and membrane formation nature is shown in Table 4.

The same method as an example 1 estimated the physical property and **** property of an ink constituent. After ****, in the room temperature and the vacuum, membrane formation nature removed the solvent, among nitrogen-gas-atmosphere mind, 150 degrees C, is what was processed for 4 hours, and evaluated it.

[0082]

[Table 4]

粘度 [mPa·s]	3.21
表面張力 [mN/m]	37.8
接触角 [°]	58.6
目詰まり頻度 [sec]	>10000
飛行ばらつき [μ m]	±25
パターニング性	⊕
成膜性	⊕

[0083] As shown in Table 4, it was that to which *****, patterning nature, and membrane formation nature reach sufficiency and practical use level. On the other hand, although it was satisfactory to ***** for example, when the ink constituent which replaced butyl carbitol acetate (BCA) with the glycerol was prepared and the same membrane formation and same evaluation as the above were performed or it replaced DMI by the dimethylformamide (DMF), luminous efficiency was low and also shifted the luminescent color to the short wavelength side. the case where he wants to make solid part concentration deeper than 0.3wt(s)% -- a precursor solution -- more than 20wt% -- if it adds -- a MeOH content -- increasing -- ink -- becoming it dry -- being easy -- since flight deflection and blinding were produced, what ****(ed) and condensed the precursor solution was used

[0084] (Example 3) An example 3 is related with the ink constituent for luminous layers.

[0085] In this example, what added the rhodamine 101 which is a low-molecular fluorochrome as a red luminescent material was used for the PPV precursor ink constituent used in the example 2.

[0086] The method of doping the fluorochrome of a low-molecular system can change the luminescence property of a luminous layer, for example, is very effective considering the improvement in luminous efficiency, or luminescence wavelength as a frog means. The high red of color purity and green luminescence can be obtained by the dope of a fluorochrome.

[0087] As a fluorochrome used for a red luminous layer, DCM of laser coloring matter, a rhodamine or a rhodamine derivative, a perylene, etc. can be used. Since it is low-molecular, it is meltable to a solvent, and these fluorochromes have PPV etc. and good compatibility and formation of the uniform and stabilized luminous layer is easy for them. As a rhodamine derivative fluorochrome, Rhodamine B, the Rhodamine B base, rhodamine 6G, rhodamine 101 perchlorate, etc. are mentioned, for example, and two or more sorts of these may be mixed.

[0088] Moreover, as a fluorochrome used for a green luminous layer, a Quinacridone, rubrene, DCJT(s), and those derivatives are mentioned. Like the above-mentioned red fluorochrome, since these fluorochromes are low-molecular, PPV etc. and compatibility are good meltable and formation of a luminous layer is easy for them to a solvent.

[0089] In this example, the ink constituent for red luminous layers shown in the following table 5 was prepared.

[0090]

[Table 5]

組成物	材料名	含有量 (wt%)
発光材料	PPV前駆体溶液 (1.5wt%)	20
	(水/メタノール=5/95 混合溶液)	
	ローダミン101	0.0045
		前駆体固型分比 1.5wt%
極性溶媒	1,3-ジメチル-2-イミダゾリジノン	70
	ブチルカルビトールアセテート	10

[0091] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink **** nozzle side of the head for ink jets, *****, patterning nature, and membrane formation nature is shown in Table 6. The same method as an example 2 estimated the physical property of an ink constituent and a **** property, and membrane formation nature.

[0092]

[Table 6]

粘度 [mPa·s]	3.27
表面張力 [mN/m]	37.4
接触角 [°]	60
目詰まり頻度 [sec]	>10000
飛行ばらつき [μm]	±25
パターニング性	◎
成膜性	◎

[0093] As shown in Table 6, it was that to which *****, patterning nature, and membrane formation nature reach sufficiency and practical use level. the amount of dopes of a rhodamine 101 -- a PPV precursor -- receiving -- 1.5wt(s)% -- when it added, it was the most efficient and red luminescence was shown

[0094] (Example 4) An example 4 is related with the manufacture method of the organic EL element by the ink-jet method. Drawing 4 shows the manufacturing process of the full color organic EL element of three colors.

[0095] While the transparent substrate 104 is a base material, it functions as a field which takes out light. Therefore, the transparent substrate 104 is chosen in consideration of the transparency property and thermal stability of light. As a transparent substrate material, although a glass substrate, transparent plastics, etc. are mentioned, for example, since it excels in thermal resistance, a glass substrate is desirable.

[0096] First, the pixel electrodes 101, 102, and 103 were formed on the transparent substrate 104. As the formation method, although photo lithography, vacuum deposition, the sputtering method, the metal-fog method, etc. are mentioned, for example, being based on photo lithography is desirable. As a pixel electrode, a transparent pixel electrode is desirable, and a tin oxide film, an ITO film, the multiple-oxide film of indium oxide and a zinc oxide, etc. are mentioned as a material which constitutes a transparent pixel electrode.

[0097] Next, the septum (bank) 105 was formed by the photosensitive polyimide, and it buried each above transparent pixel inter-electrode. Thereby, improvement in contrast, prevention of the color mixture of luminescent material, the optical leak from between a pixel and pixels, etc. can be prevented.

[0098] although it obtains, and it will not be limited especially if it is, organic materials, such as acrylic resin, an epoxy resin, and a photosensitive polyimide, are desirable, for example from the thing which have endurance to the solvent of EL material as a material which constitutes a septum 105 and for which-izing can be carried out [Teflon] by fluorocarbon gas plasma treatment You may be the laminating septum which made inorganic material, such as liquefied glass, the lower layer. Moreover, a septum 105 mixes carbon black etc. in the above-mentioned material, and is good also as a black resist. As the formation method of this septum 105, photo lithography etc. is mentioned, for example.

[0099] Just before applying the ink constituent for hole-injection layers (further electron hole transporting bed), continuation plasma treatment of the oxygen gas of the above-mentioned substrate and fluorocarbon gas plasma was performed. Thereby, **** and an ITO front face are hydrophilicity-ized and a polyimide front face can perform wettability control by the side of the substrate for carrying out patterning of the ink-jet drop minutely. As equipment which generates plasma, it can use similarly with the equipment which generates plasma in a vacuum, or the equipment which generates plasma in the atmosphere.

[0100] Next, the ink constituent for hole-injection layers mentioned in the example 1 was breathed out from the head 110 (Epson MJ-930C) of ink-jet print equipment 109, and the patterning application was performed on each pixel electrodes 101 and 102 and 103. The solvent was removed on a room temperature and the conditions of 20 minutes after an application and among the vacuum (1torr), and the ink constituent for luminous layers mentioned in the examples 2 and 3 and the hole-injection layer 120 not dissolving were formed among the atmosphere after that with 200 degrees C (on a hot plate), and heat treatment for 10 minutes. Thickness was 40nm. Although each pixel formed the common hole-injection layer in this example, depending on the case, you may form using the hole-injection material (or electron hole transportation material) which was suitable for the luminous layer the whole luminous layer.

[0101] The ink constituent for red luminous layers furthermore mentioned in the example 3 and the ink constituent for green luminous layers mentioned to the row in the example 2 were applied to the pixel electrode 101 row in the shape of PATANIN on 102 through the hole-injection layer 120 top with the ink-jet method. After an application and among the vacuum (1torr), the solvent was made to remove and conjugate continuously with 150 degrees C and heat treatment of 4 hours among nitrogen-gas-atmosphere mind on a room temperature and the conditions of 20 minutes, and the red luminous layer 106 and the green luminous layer 107 were formed. Thickness was 50nm. The luminous layer conjugated with heat treatment is insoluble to a solvent.

[0102] According to this ink-jet method, detailed patterning can be performed simple in a short time. Moreover, it is possible by changing the solid part concentration and discharge quantity of an ink constituent to change thickness.

[0103] Moreover, before forming a luminous layer, you may perform continuation plasma treatment of oxygen gas and fluorocarbon gas plasma in the hole-injection layer 120. A fluorine ghost layer is formed on a hole injection or the electron hole transporting bed 120 by this, and ionization potential can offer the increase of hole-injection efficiency, and the organic high EL element of luminous efficiency by the bird clapper highly.

[0104] Subsequently, the blue luminous layer 108 was formed on the pixel electrode 103 through the red luminous layer 106, green luminous layer 107, and hole-injection layer 120 top. Thereby, it not only forms the three primary colors of red, green, and blue, but it can bury and carry out flattening of the level difference of a red luminous layer and the 106 green luminous layer 107, and a septum 105. Thereby, vertical inter-electrode short-circuit can be prevented certainly. By adjusting the thickness of a blue luminous layer, in a laminated structure with a red luminous layer and a green luminous layer, a blue luminous layer acts as an electron-injection transporting bed, and does not emit light blue.

[0105] It is not limited especially as the formation method of this blue luminous layer 108, but membranes can be formed also by the general spin coat method as a wet method, or the ink-jet method. In this example, the spin coat of the xylene solution of the poly dioctyl fluorene was carried out, and the blue luminous layer 108 of 45nm of thickness was formed.

[0106] The poly dihexyl fluorene which is otherwise the poly fluorene derivative as a blue luminous layer, and a copolymer with other polymerization machines are mentioned, and an organic compound with a blue fluorochrome or electron-injection transportation ability may be added.

[0107] As an organic compound which can form an electron-injection transporting bed, PBD, the OKISA diazole derivative of OXD-8 grade, DSA, an aluminum quinol complex, Bebq, a triazole derivative, an azomethine complex, a porphin complex, etc. are mentioned.

[0108] Since a full color organic EL element can be formed by combining with other organic luminescent material used for an ink-jet method even if it is the luminescent material which is seldom suitable for an ink-jet method by forming two colors with an ink-jet method among organic luminous layers, and forming other Isshiki by the conventional method of application like

this example, the flexibility of an element design increases. As the conventional methods of application other than an ink-jet method, print processes, a replica method, a dipping method, the spin coat method, the cast method, the capillary-tube method, the roll coat method, the bar coat method, etc. are mentioned.

[0109] Finally, cathode (counterelectrode) 113 was formed. As cathode 113, a metal thin film electrode is desirable, and Mg, Ag, aluminum, Li, etc. are mentioned as a metal which constitutes cathode, for example. Moreover, the alloy which can use a small material of a work function other than these, for example, contains alkali metal, alkaline earth metal, such as calcium, and these can be used. Moreover, a metaled fluorine ghost can also be adapted. Such cathode 113 can be formed by the vacuum deposition, the spatter, etc. In this example, calcium was carried out by the vacuum heating vacuum deposition, 1200nm laminating of the 100nm of the aluminum was further carried out by the spatter, and it considered as cathode.


[0110] Furthermore, you may form a protective coat on cathode 113. By forming a protective coat, cathode 113 and degradation of each luminous layers 106, 107, and 108, damage, exfoliation, etc. were able to be prevented.

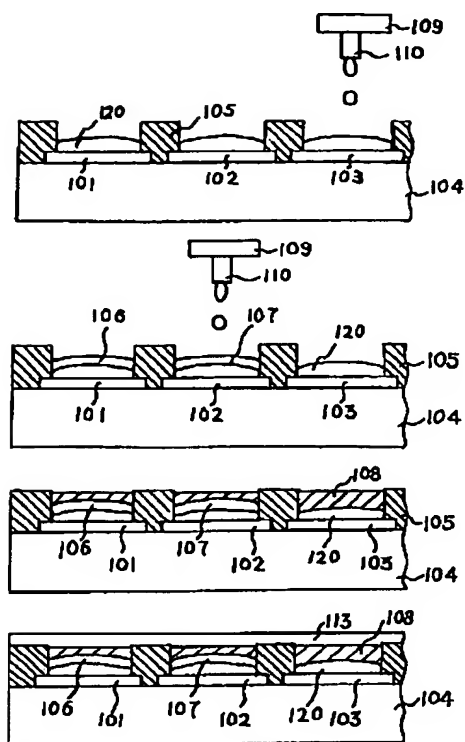
[0111] As a component of such a protective coat, an epoxy resin, acrylic resin, liquefied glass, etc. are mentioned. Moreover, as the formation method of a protective coat, the spin coat method, the casting method, a dipping method, the bar coat method, the roll coat method, the capillary-tube method, etc. are mentioned, for example.

[0112] In the organic EL element obtained by this example, two or more 100 cd/m brightness was obtained [the low battery not more than 5V] for the pixel of each color. Moreover, in the red pixel and green pixel which were formed with the ink-jet method, luminous efficiency was 0.15 lm/W and 0.25 lm/W, respectively, and the luminescence life (time when continuation luminescence is carried out, until it impresses fixed current, and it falls 50% to initial brightness) was also 2000 hours or more.

[0113] It was of the same grade as the thing of the red light emitting device which formed the hole-injection layer and the luminous layer by the same laminated structure on the spin coat using the same material as the above, and a green light emitting device. Thus, the property which was excellent also in the ink-jet method was able to be shown, and the element which is not inferior to a spin coat article was able to be formed.

[Translation done.]

Drawing selection [R presentative drawing] 



[Translation done.]

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JAPANESE

[JP,2000-323276,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the flat-surface perspective diagram showing an example of the structure of the printer head for ink jets used for manufacture of the organic thin film EL element of this invention.

[Drawing 2] It is the cross section showing an example of the structure of the nozzle portion of the printer head for ink jets used for manufacture of the organic thin film EL element of this invention.

[Drawing 3] In the example of this invention, it is drawing showing the patterning nature of an ink constituent, and the test cell used for membrane formation nature evaluation.

[Drawing 4] It is the cross section showing an example of the manufacture method of the organic EL element of this invention.

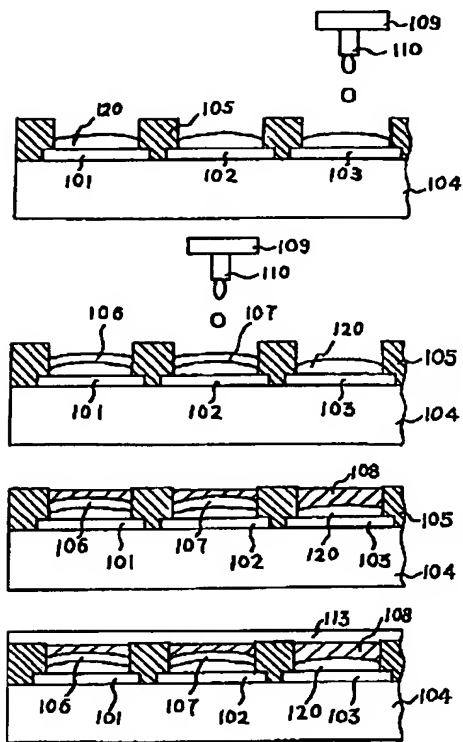
[Description of Notations]

- 10 Head for Ink Jets
- 11 Nozzle Plate
- 13 Diaphragm
- 15 Batch -- Member
- 19 Ink Room
- 21 *****
- 23 Feed Hopper
- 25 Nozzle -- Hole
- 26 ** Ink Layer
- 27 Ink Introduction -- Hole
- 29 Piezoelectric Device
- 31 Electrode
- 33 Nozzle Side
- 40 Polyimide Septum
- 41 ITO
- 42 Ink-Jet Print Equipment
- 43 Ink-Jet Head
- 44 Ink Constituent
- 101 Pixel Electrode (Red)
- 102 Pixel Electrode (Green)
- 103 Pixel Electrode (Blue)
- 104 Transparent Substrate
- 105 Septum
- 106 Luminous Layer (Red)
- 107 Luminous Layer (Green)
- 108 Luminous Layer (Blue)

109 Ink-Jet Print Equipment
110 Ink JIETO Head
113 Cathode
120 Hole-Injection Layer

[Translation done.]

Drawing selection [Representativ drawing] 



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JAPANESE

[JP,2000-323276,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

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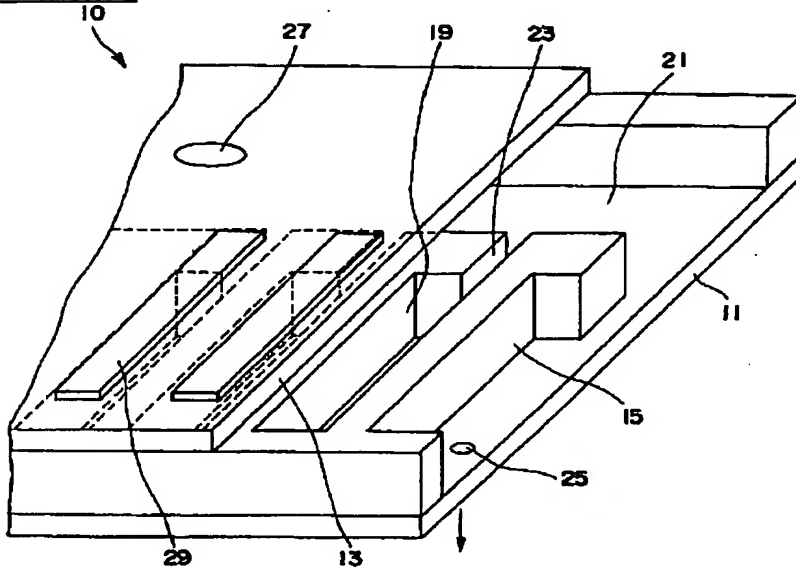
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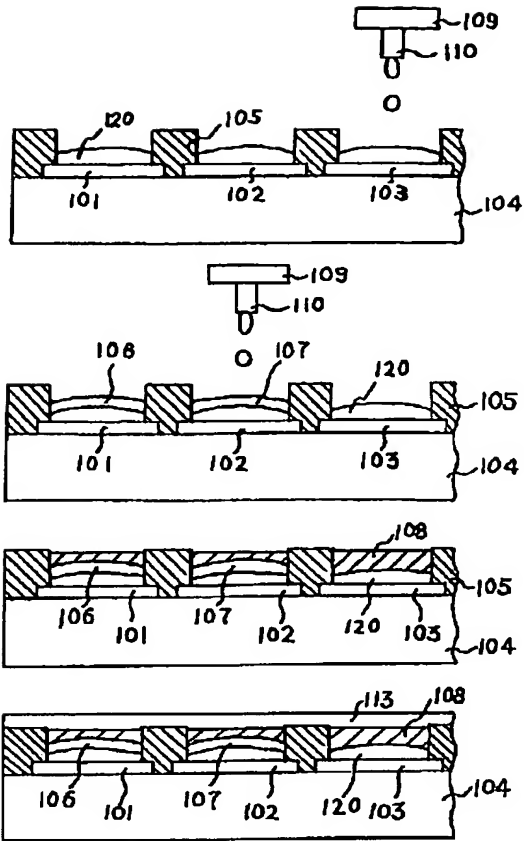
3.In the drawings, any words are not translated.

DRAWINGS

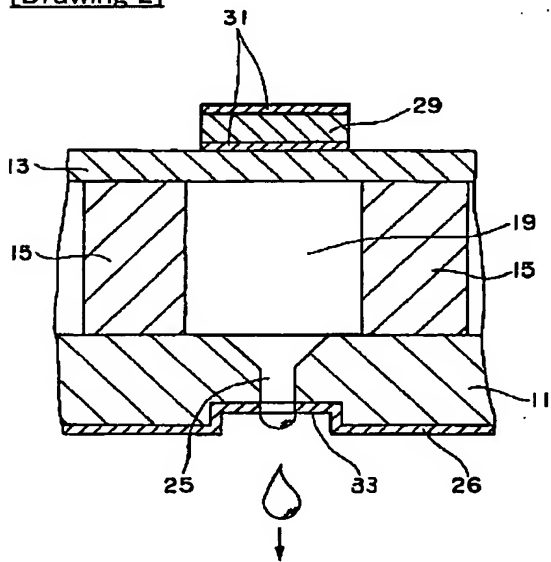
[Drawing 1]



[Drawing 4]

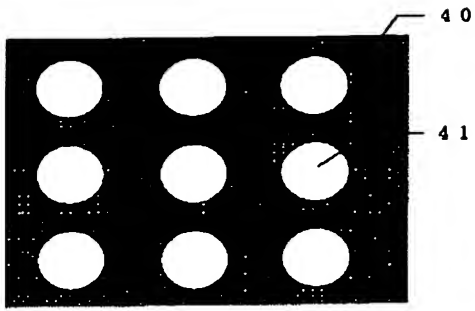


[Drawing 2]

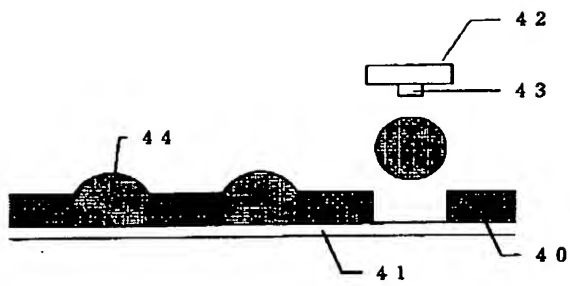


[Drawing 3]


(a)

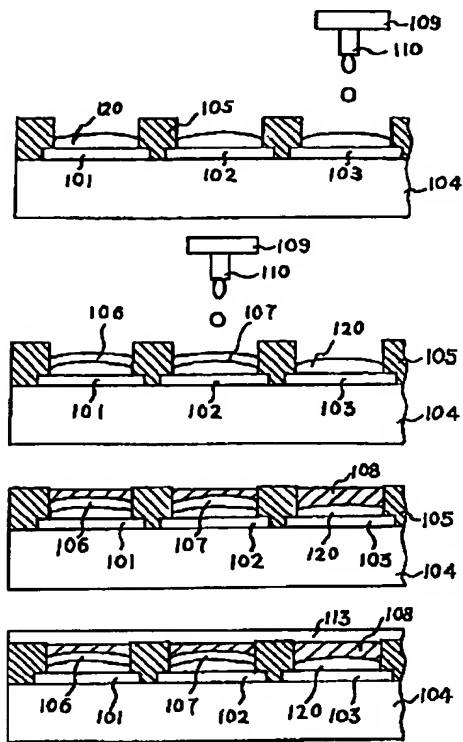


(b)



[Translation done.]

Drawing selection [R pr sentativ drawing] 



[Translation done.]

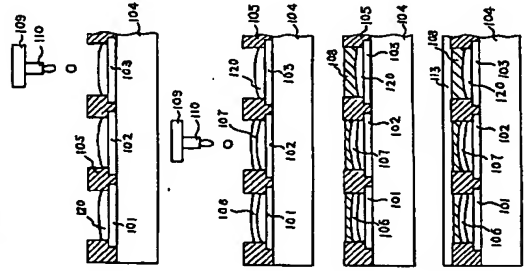
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(51) InCl ⁺	識別記号	P I	573-1 (参考)
H 0 5 B 33/10		H 0 5 B 33/10	3 K 0 0 7
G 0 9 F 9/30	3 6 5	G 0 9 F 9/30	5 C 0 9 4
H 0 5 B 33/12		H 0 5 B 33/12	3 6 5 B B
33/14			A
33/22		33/14	Z
		33/22	

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(54) 【発明の名称】 有機EL素子の製造方法、有機EL素子およびインク組成物

(57) 【要約】
【課題】有機揮発性EとE₂の簡便かつ容易な製造方法を提供すること。
【解決手段】正孔注入層(120)と発光層(106、107)を、絶縁(101)および陰極(113)で挟持した発光の有機EとE₂の製造方法であって、絶縁上(120)の所定の領域に有機化合物からなる正孔注入材料を含むインキング組成物をインクジェット方式により塗布し正孔注入層(120)を形成する工程と、有機化合物からなる発光材料を含むインク組成物をインクジェット方式により塗布し発光層(106、107)を形成する工程とを具備することを特徴とする。



ク組成物。

【請求項25】 前記インク組成物が発光材料を含むものであり、該発光材料として、ポリ（パラフェニレンビニレン）およびその誘導体の前駆体を含むことを特徴とする請求項17記載のインク組成物。

【請求項26】 前記発光材料として低分子色素をドーブしたものを使用することを特徴とする請求項25記載のインク組成物。

【発明の詳細な説明】

【0001】
【発明の属する技術分野】 ディスプレイ、表示装置などに用いられる電気的発光素子である有機EL素子の製造方法、有機EL素子、その正孔注入層や発光層の形成に用いられるインク組成物に関する。

【0002】
【従来の技術】 近年液晶ディスプレイに替わる自発発光型ディスプレイとして発光層に有機物を用いた発光素子の開発が加速している。有機EL（エレクトロルミネッセンス）素子における有機物からなる発光層の形成プロセスとして、Appl. Phys. Lett. 51 (1987) 21 September 1987の913ページに示されているように低分子材料を蒸着法で形成する方法と、Appl. Phys. Lett. 71 (1997) 34 July 1997の34ページに示されているように低分子材料を塗布する方法が主に開発されている。

【0003】 カラー化の手段としては低分子系材料を用いる場合、所定パターンのマスク越しに異なる発光色の発光材料を所定の画素毎に蒸着して形成する方法が行われている。一方、高分子系材料を用いる場合、微細かつ容易にパターンニングができることからインクジェット法を用いたカラー化が注目されている。インクジェット法による有機EL素子の作製については、例えば、特開平7-235378、特開平10-12377、特開平10-153987、特開平11-40358、特開平11-54270に開示されている。

【0004】 さらに有機EL素子では、発光効率、耐久性を向上させるために、正孔注入層または正孔輸送層を有機物と発光層の間に形成することが提示されている（Appl. Phys. Lett. 51, 21 September 1987の913ページ）。従来、バンプ層や正孔注入層としては導電性高分子、例えばポリオフェン誘導体やポリアニリン誘導体（Nature, 357, 477, 1992）を用い、スピンコート等の塗布法により膜を形成する。低分子系材料の正孔注入層または正孔輸送層として、フェニルアミン誘導体を蒸着で形成して用いることが多かった。

【0005】
【発明が解決しようとする課題】 有機EL素子において、正孔注入層及び発光層の層構造を形成する際に、

正孔注入層及び発光層を構成する有機誘導体を無抵抗にせず、堅固にかつ微細にパターンニングして成膜する手段が要求されている。

【0006】 インクジェット方式は大変有効である。しかし、インクジェット法による安定な吐出性を満たし、かつ材料の特性を損なわずに機能膜として成膜できるインク組成物の開発は大変難しい課題である。有機EL素子の製造においては、インク組成物については特開平11-40358、特開平11-54270に記載されている。

【0007】 また、パターンニングの分解能を上げたため、ノズル径を小さくし、より小さなインクジェット液滴を形成しようとする、液滴が小さくならないようなインクは乾きやすくなるという問題も生じている。

【0008】 さらに、インクジェット法のみならず塗布法で有機物を塗布する場合、組成物の溶媒が下地の有機物を溶解する、いわゆる相溶性の問題となる。具体的には正孔注入層（または正孔輸送層）の上に発光層を形成する場合である。

【0009】 そこで本発明の課題とするところは、簡便、短時間、低コストで特性の優れた有機層を形成からなる有機EL素子を製造する方法ならびにそれを可能にするインク組成物を提供することにある。

【0010】
【課題を解決するための手段】 本発明によれば、下記（1）～（5）の有機EL素子の製造方法が提供される。

【0011】 （1）正孔注入層と発光層を、有機物および誘導体で支持した構造の有機EL素子の製造方法であって、基板上の所定の領域に有機化合物からなる正孔注入層を含むインク組成物をインクジェット方式により塗布し、発光層を形成する工程とを具備することを特徴とする有機EL素子の製造方法。

【0012】 当該方法は有機化合物からなる正孔注入層及び発光層の両方をインクジェット方式で形成したものである、かかる方法により、簡便な方法で全ての有機物を形成することができ、またいずれの層も高い性能とすることができ。

【0013】 尚、本発明において、正孔注入層とは、基盤から発光層に有効に正孔を注入させ得る層であり、

正孔輸送機能をも有する。また、正孔注入層と共に、正孔輸送機能を有する正孔輸送層を別層で設けてもよい。

【0014】 （2）有機EL素子が基板上に複数の画層を有する素子であり、基板上に複数の画層を有する素子であり、基板上に複数の画層を有する素子の製造方法。

【0015】 当該（2）の方法により、異なる発光層が混合することなく、多色で且つ高解像度の有機EL素子を容易に得ることができる。

【0016】 （3）有機EL素子が基板上に複数の画層を有する素子であり、基板上に複数の画層を有する素子の製造方法。

【0017】 当該（3）の方法により、基板上に液滴の濡れ性の違いを付与することができ、インクジェット液滴の微細パターンニングが可能となる。

【0018】 （4）前記有機化合物からなる正孔注入層を含むインク組成物のインクジェット方式により塗布した後、該インク組成物の溶媒を除去して、正孔注入層を得ること、及び前記有機化合物からなる発光材料を含むインク組成物をインクジェット方式により塗布した後、該インク組成物の溶媒を除去し、発光層を得ることを特徴とする（1）の有機EL素子の製造方法。

【0019】 当該（4）の方法により所定の特性の正孔注入層及び発光層としての有機固体薄膜を形成することができ。

【0020】 （5）前記有機化合物からなる正孔注入層を含むインク組成物をインクジェット法により塗布した後、さらに熱処理により該インク組成物の材料を硬化あるいは非酸化させて正孔注入層を得ること、及び前記有機化合物からなる発光材料を含むインク組成物をインクジェット方式により塗布した後、さらに熱処理により該インク組成物の材料を硬化あるいは非酸化させて発光層を得ることを特徴とする（1）の有機EL素子の製造方法。

【0021】 当該（5）の方法により、優れた機能を有する正孔注入層および発光層を形成できる。

【0022】 また、本発明によれば、下記（6）乃至（15）のインク組成物が提供される。（6）有機EL素子の製造においてインクジェット法により塗布される正孔注入層又は発光材料を含むインク組成物であって、粘度が1～20 mPa・s、表面張力が20～70 mN/m、インクジェットヘッドのノズル径を構成する材料に対する接触角が30～170°であることを特徴とするインク組成物。

【0023】 当該（6）のインク組成物によれば、特にインクジェット法により塗布する場合に、ノズル孔の目詰まりを防止する。

詰まり、インク液滴の飛行曲がりを押さえるとともに吐出を円滑にし、吐出量および吐出タイミングの調節が可能となり、インクジェット方式による安定な吐出が可能となる。

【0024】 （7）固型分濃度が0.01～10.0 wt %であることを特徴とする（6）のインク組成物。

【0025】 当該（7）のインク組成物によれば、インクジェット法により塗布する場合に、吐出性を損なうことなく所望の膜厚を得ることが可能となる。

【0026】 （8）蒸気圧が0.001～50 mmHg（室温）の少なくとも一種の溶媒を含むことを特徴とする（6）又は（7）のインク組成物。

【0027】 当該（8）のインク組成物によれば、インクジェット法により塗布する際に、インクの乾きを抑えることができ、ノズル孔の目詰まりをなくすることができ。

（9）前記インク組成物の溶媒が非プロトン性溶媒であることを特徴とする（8）のいずれかのインク組成物。

【0028】 当該（9）のインク組成物は、正孔注入材料あるいは発光材料の特性を損ねることなく、安定な分散液または溶液、インクジェット法により塗布する際に安定な吐出が可能となる。

【0029】 （10）グリコールエーテル系溶媒を含むことを特徴とする（6）乃至（9）のいずれかのインク組成物。

【0030】 当該（10）のインク組成物によれば、インクの乾きを抑えることができるだけでなく、成膜性を向上させることができる。

【0031】 （11）低級アルコールを20 wt %以下含むことを特徴とする（6）乃至（10）のいずれかのインク組成物。

【0032】 当該（11）のインク組成物によれば、特にインクジェット法により塗布する際に、インクの吐出性を損ねることなく表面張力および粘度を所望の値に調整することが可能となる。

【0033】 （12）前記インク組成物が正孔注入材料を含むものであり、該正孔注入材料としてポリオフェン誘導体とポリスチレンスルホン酸の混合物を含むことを特徴とする（6）のインク組成物。

【0034】 当該（12）のインク組成物によれば、特にインクジェット法により塗布する際に、吐出性、成膜性ともに優れ、有機EL素子において高性能の正孔注入層を得ることが可能となる。

【0035】 （13）更に熱硬化剤としてシランカップリング剤を含むことを特徴とする（12）のインク組成物。

【0036】 当該（13）のインク組成物を用いれば、特にインクジェット法により塗布することで、有機EL素子において発光層との相溶を起こさない正孔注入層を形成する。

【0064】の重合物を用いた。これらはバイトロンプとしてバイエセル社から購入することができる。正孔注入剤としてバイエセル社の材料となる正孔輸送材料として、ポリアニリン、ポルフィリン化合物、ピリジン誘導体などが挙げられるが、熱的に耐久性のある高分子【0065】

組成物	材料名	含有量 (wt%)
正孔注入剤/電解質材料	PEOT (PFSS) (バイトロンプ) (本分濃度)	7.25
電解質材料	水	52.75
	イソノール	5
	イソプロピルアルコール	5
	1,3-ジエチル-2-イソチアゾリジン	20
シランカップリング剤	1,3-ジエチル-2-イソチアゾリジン	0.05

【0066】発光層との相溶を防ぐため、加熱処理により架橋するシランカップリング剤としてγ-グリジリルオキシプロピルトリメトキシシランを用い、導電性高分子と同等量添加した。最終的なインク組成物の固型分濃度は0.16wt%であった。

【0067】表2に上記組成物の粘度、表面張力、インクジェット用ヘッドのインク吐出ノズル面を構成する材料に対する接触角、吐出性、バクテリアン性および成膜性を評価した結果を示す。インク組成物の物理的性質および吐出特性については以下の方法で評価した。

【0068】粘度：E型粘度計により20℃における値を測定した。

【0069】表面張力：プレート法により同じく20℃における値を測定した。

【0070】接触角：インクジェット用ヘッドのインク吐出ノズル面を構成する材料（N1-テトラフルオロエチレン非所、ツキ精水層）上での静的接触角として測定した。

【0071】吐出特性：インクジェットプリンター用ヘッド（エプソン社製MJ-930C）を用いた。飛行曲上でのインク液滴の直径は0.6mmにした時の直径の目盛より測定し、インク組成物を連続吐出（周波数7200Hz）し、析出したインク組成物の固型分率によりノズル孔が目詰まりし、吐出不能になった状態に至るまでに要する時間を測定した。

【0072】バクテリアン性、成膜性：図3(a)及び(b)に示したテストセルに吐出し、室温、真空中で乾燥を除去した後、大気中20℃、10分乾燥処理して形成された膜の厚さ（乾燥、平坦性等）を顕微鏡で観察した。テストセルはITO基板41上に形成した2μm厚のポリイミド40を30μm径で開口した面罩（40μmピッチ）を有するものである。吐出前に、露光マスクアスマとフロロロゴンガスアスマの連続処理を行い、ポリイミド表面は脱水化、ITO表面は脱水化したものを用いた。尚、前記アスマ処理は真空中、大気中いずれの雰囲気であってもよい。そして、インクを吐出し、インクジェットヘッド43からインク組成物を吐出し、開口部に吐出し膜を得て評価した。結果を下記表4.4

組成物	粘度 (mPa·s)	表面張力 (mN/m)	接触角 (°)	吐出特性 (μm)	成膜性
表2に示すインク	2.05	44	65	>10000	◎
比較例1	2.05	44	65	>10000	◎
比較例2	2.05	44	65	>10000	◎

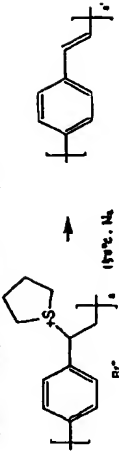
【0074】表2に示すように、吐出性、バクテリアン性、成膜性とも十分、実用レベルに達するものであった。尚、表1の組成物例えば、メタノール（MeOH）、H）、インプロピルアルコール（IPA）の添加量が20%を超える組成物を調整して上記組成物に成膜し、評価したところ、または、1,3-ジメチル-2-イミダゾリジン（DMI）を添加せず水で置き換えた組成物を調整して上記組成物に成膜して評価したところ、上記組成物の値を調製したとしても、インク組成物の値により吐出、目詰まりを起こしてしまつた。

【0075】（実施例2）実施例2は発光層用インク組成物に関する。

【0076】本発明では、緑色発光材料としてポリ（ラファエレンビニレン）（PPV）を用いた。

【0077】発光層を形成し得る有機化合物としては、PPVの他に、PTV（ポリ（2,5-チエニレンビニレン））等のポリアルキルカルボフェン、PFV（ポリ（2,5-フリレンビニレン））、ポリラファエレン、ポリアルキルフルオレン等のポリアリレンビニレン、ピラゾリンダイマー、キノリジンカルボン酸、ベンゾピリリウムクロレート、ベンゾピラノキノリジン、フェナントロリノンクロロピウム錯体等が挙げられ、これらを1種または2種以上混合して用いることができる。これらのなかでも高分子有機化合物からなるものが好ましい。高分子有機化合物は成膜性に優れ、発光層の耐久性は極めて良好である。高分子系材料は分子設計の自由度が広い。また、可視領域の禁止帯幅と比較的広い導電性である。また、可視領域の禁止帯幅と比較的広い導電性を有しており、なかでも共役系高分子はこのような傾向が顕著である。発光層材料としては、共役系高分子そ

のもの、あるいは加酸等により非酸化（成膜）する共役系分子の前提体が用いられる。これらのなかでもPPVまたはその誘導体が特に好ましい。PPV誘導体の前提体として、MO-PPV（ポリ（2,5-ジメチルシ-1,4-フエニレンビニレン））前提体、CN-PPV（ポリ（2,5-ビスヘキシルオキシシ-1,4-フエニレン）（1-シアノビニレン））前提体等が挙げられる。PPVまたはその誘導体の非酸化（成膜）の*



【0079】ポリ（ラファエレンビニレン）前提体（水/MeOH=5/95混合液）を用いて表3に示すインク組成物を調整した。固型分濃度は0.3wt%であった。【0080】

組成物	材料名	含有量 (wt%)
発光材料	PPV前提体 (1.5wt%)	20
	(水/MeOH=5/95混合液)	
電解質材料	1,3-ジエチル-2-イソチアゾリジン	70
	テトラメチルアミン	10

【0081】表4に上記組成物の粘度、表面張力、インクジェット用ヘッドのインク吐出ノズル面を構成する材料に対する接触角、吐出性、バクテリアン性および成膜性を評価した結果を示す。インク組成物の物理的性質および吐出特性については実施例1と同様の方法で評価した。成膜性は吐出後、室温、真空中で乾燥を除去し、真空中で乾燥し、150℃、4時間処理したもので評価した。

【0082】

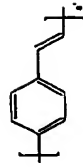
組成物	粘度 (mPa·s)	表面張力 (mN/m)	接触角 (°)	吐出特性 (μm)	成膜性
表4に示すインク	2.21	37.6	56.6	>10000	◎
比較例1	2.21	37.6	56.6	>10000	◎
比較例2	2.21	37.6	56.6	>10000	◎

【0083】表4に示すように、吐出性、バクテリアン性、成膜性とも十分、実用レベルに達するものであった。これに対し、例えば、DMIをメチルカルボミド（DMF）で置き換えた場合は、ベンゾピラノキノリジン（BCA）をグリセリンで置き換えたインク組成物を調整し上記組成物の成膜性及び評価を行ったところ、吐出性に問題がなかったが、発光効率が低く、発光色も短波長側にシフトしたものであった。固型分濃度を0.3wt%より高くした場合は、前提体濃度を0.4wt%以上添加するとMeOH含有率が上がり、インクが過剰になり、飛行曲がやや目詰まりを生じるとめ、前提体濃度を低減して調整したものを示した。

*前提体は、水あるいは酸性溶液中に可溶であり、インクジェット方式によるバクテリアン形成に適している。さらに、PPVまたはその誘導体は強い蛍光を持ち、二重結合のπ電子がリナール一面上で非局在化している導電性高分子でもあったPPVの誘導体は正孔注入輸送層としても機能し、成膜性の向上に寄与することができる。

【0078】

【化3】



【0084】（実施例3）実施例3は発光層用インク組成物に関する。

【0085】本実施例では、表2で用いたPPV前提体インク組成物に緑色発光材料として低分子発光色素であるローザミン101を添加したものを示した。

【0086】低分子系の発光色素をドープする方法は、発光層の発光特性を変化させることができ、例えば、発光効率の向上、または発光波長を可変手段として大発色、緑色発光を得ることができる。

【0087】緑色発光層に用いられる発光色素としては、ローザミン101あるいはローザミン101はロザミン誘導体、ペリレン等を用いることができる。これらの発光色素は、低分子であるため溶媒に可溶であり、PPV等と相溶性がよく、均一で安定した発光層の形成が容易である。ローザミン誘導体発光色素としては、例えばローザミンB、ローザミンベーズ、ローザミン6G、ローザミン101誘導体等が挙げられ、これらを2種以上混合したものであってもよい。

【0088】また、緑色発光層に用いられる発光色素としては、キノリジン、ルピレン、DCJTおよびそれらの誘導体が挙げられる。これらの発光色素は、上記発光色素と同様、低分子であるため溶媒に可溶であり、またPPV等と相溶性がよく発光層の形成が容易である。

【0089】本実施例では、下記表5に示す赤色発光層用インク組成物を調整した。

50 【0090】

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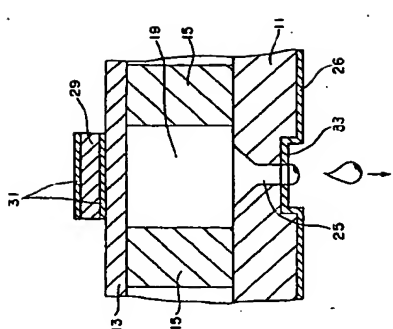
ある。

【図4】本発明の有機EL素子の製造方法の一例を示す断面図である。

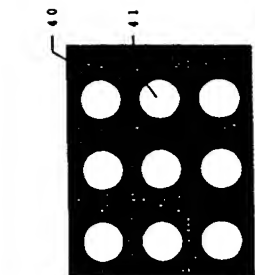
【符号の説明】

- 10 インクジェット用ヘッド
- 11 ノズルプレート
- 13 駆動板
- 15 仕切部材
- 19 インク室
- 21 液溜り
- 23 供給口
- 25 ノズル孔
- 26 原インク層
- 27 インク導入孔
- 29 圧電素子
- 31 電極
- 33 ノズル面
- 40 ポリイミト隔壁
- 41 ITO
- 42 インクジェットプリント装置
- 43 インクジェットヘッド
- 44 インク組成物
- 101 画素電極 (赤)
- 102 画素電極 (緑)
- 103 画素電極 (青)
- 104 透明基板
- 105 隔壁
- 106 発光層 (赤)
- 107 発光層 (緑)
- 108 発光層 (青)
- 109 インクジェットプリント装置
- 110 インクジェットヘッド
- 113 陰極
- 120 正孔注入層

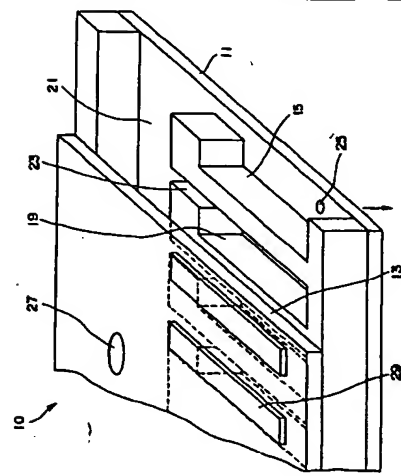
【図2】



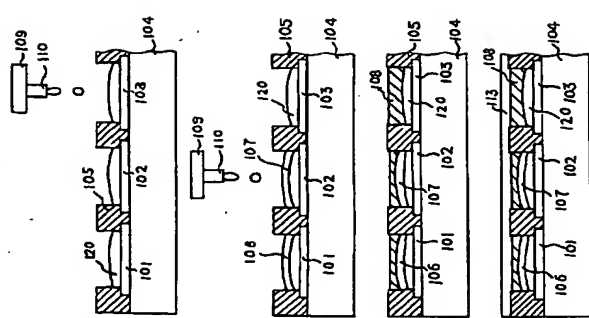
【図3】



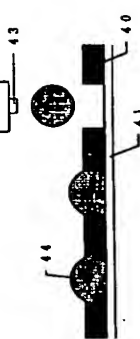
【図1】



【図4】



【図(b)】



フロントページの続き

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